



INSTITUTE OF HEALTH SCIENCES

FACULTY OF PUBLIC HEALTH

DEPARTMENT OF ENVIRONMENTAL HEALTH SCIENCES AND TECHNOLOGY

TITLE: ADSORPTIVE REMOVAL OF DIRECT BLACK 22 DYE USING PUMICE
AND SCORIA FROM AQUEOUS SOLUTION AND WASTEWATER

BY

ADDISU DUGASA

A THESIS SUBMITTED TO DEPARTMENT OF ENVIRONMENTAL HEALTH
SCIENCE AND TECHNOLOGY, INSTITUTE OF PUBLIC HEALTH, JIMMA
UNIVERSITY, IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE
DEGREE OF MASTER OF SCIENCE IN ENVIRONMENTAL SCIENCE AND
TECHNOLOGY

NOVEMBER 2018

JIMMA, ETHIOPIA

ADSORPTIVE REMOVAL OF DIRECT BLACK 22 DYE USING PUMICE AND
SCORIA FROM AQUEOUS SOLUTION AND WASTEWATER

BY

ADDISU DUGASA

ADVISORS:

1. KASAHUN EBA (MSc, PhD CANDIDATE)
2. HAILU ENDALE (MSc, PhD CANDIDATE)

OCTOBER 2018

JIMMA, ETHIOPIA

Jimma University

Faculty of Public Health, Department of Environmental Health Science and Technology

Environmental Health Science and Technology (MSc) Program

Board of Examination Thesis Approval Sheet

Members of Board of Examiners

Name of External Examiner

signature

date

Name of Internal Examiner

Name of moderator

ACKNOWLEDGEMENTS

First, I want to thank the Almighty God. Next, I would like to express my deepest gratitude and appreciation to my advisor Mr. Kasahun Eba for his absolute encouragements and provision of constructive comments, guidance, consistent suggestions, and criticisms to direct me in the right way throughout my research work.

I would also like to thank Mr. Hailu Endale, Mr. Memberu Yetberek, Dr. Fikadu Melak, Mr. Seyoum Derib, Mr. Kebede Takele, Mr. Lenco Takele, Mr. Mohammedgezali Ibrahim, Mr. Firomsa Bidira who assisted me to get what I wanted and work smoothly my research in laboratory.

I would also like to thank Ayka Addis Textile factory, especially the dyeing unit supervisor Mr. Ali, who helped me a lot in obtaining the appropriate sample.

Furthermore, Jimma University Institute of Public Health Sciences, department of Environmental Health Science and Technology is properly acknowledged for giving me this golden and educating opportunity.

LIST OF ACRONYM AND ABBREVIATIONS

BOD: Biological oxygen demand

COD: Chemical oxygen demand

DB 22: direct black 22

EEPA: Ethiopian Environmental Protection Authority

EPA: Environmental Protection Agency

FTIR: Fourier-Transform Infrared Spectroscopy

HCl: Hydrochloric acid

HDTMA: hexadecyltrimethylammonium

LD50: Lethal Dose at 50%

mg/L: milligram per liter

NaOH: Sodium hydroxide

NS: Not Specified

NTU: Nephelometric Turbidity Units

pH: power of Hydrogen

rpm: revolution per minute

SEM: Scanning Electron Microscope

WHO: World Health Organization

XRF: X-Ray Fluorescence

Table of Contents

ACKNOWLEDGEMENTS	i
LIST OF ACRONYM AND ABBREVIATIONS	ii
List of Figures	vi
List of Tables.....	viii
Abstract	ix
CHAPTER ONE	1
1. INTRODUCTION	1
1.1 Background of the study.....	1
1.2 Statement of the problem	2
1.3. Significance of the study	4
1.4. Research questions	5
CHAPTER TWO	6
2. LITERATURE REVIEW.....	6
2.1 History of synthetic dyes	6
2.2. Processing steps in a textile industry.....	6
2.3. Chemistry of dye	7
2.4. Sources of dye Contaminations	9
2.5. Types of dye	9
2.6. Toxicity of dye and mobility in the environment.....	10
2.7. Dye removal technologies	10
2.7.1. Types of adsorption	11
2.8. Properties of Pumice and scoria	11
2.9. Characterization of adsorbents	11
2.10. Effect of pH solution and adsorption mechanism of pumice and scoria.....	12
2.11. Adsorption process	13
CHAPTER THREE.....	14
3. OBJECTIVE	14
3.1 General Objective.....	14
3.2 Specific Objective	14
CHAPTER FOUR.....	15

4. MATERIALS AND METHODOLOGY	15
4.1. Study Design	15
4.2. Study variables	15
4.3. Instrument and Apparatus.....	15
4.4. Chemicals	15
4.5. Adsorbent collection and preparation.....	16
4.6. Preparation of dye solution.....	17
4.7. Collection of real sample solution.....	17
4.8. Adsorption Procedures of synthetic dye.....	18
4.8.1. Determination of Adsorption Efficiency	18
4.8.2. Effect of Contact Time	18
4.8.3. Effect of pH solution	19
4.8.4. Effect Initial Concentration of direct black 22 dye	19
4.8.5. Effect of Dose.....	19
4.8.6. Effect of agitation time.....	19
4.9. Adsorption isotherms	19
4.9.1. Langmuir isotherm.....	20
4.9.2. Freundlich isotherm	20
4.10. Adsorption kinetics.....	21
4.10.1. Pseudo first order kinetics.....	22
4.10.2. Pseudo second order kinetics	22
4.10.3 Intra-particle Diffusion	22
4.11. Adsorption of interfering anions and real sample	22
4.12. Desorption Studies	23
4.13. Statistical analysis	23
4.14. Quality Control.....	23
5. RESULTS AND DISCUSSION	24
5.1. Effect of Contact Time	24
5.2. Effect of pH on adsorption mechanism.....	25
5.3. Effect of Initial Concentration of direct black 22 dye.....	28
5.4. Effect of Adsorbent Dose	29

5.5. Effect of Agitation Time	31
5.6. Adsorption Isotherm Study	32
5.7. Adsorption Kinetics Study	35
5.7.1. Pseudo first order kinetics.....	35
5.7.2. Pseudo second order kinetics	36
5.7.3 Intra-particle diffusion	39
5.8. Effect of interfering ions	40
5.9. Applicability of pumice and scoria as adsorbents in Textile real sample	41
5.10. Desorption of direct black 22 dye from pumice and scoria Surfaces.....	43
CHAPTER SIX	45
6. CONCLUSION AND RECOMMENDATION	45
6.1. Conclusion.....	45
6.2. Recommendation.....	46
7. References	i
Appendix.....	i
Appendix ii.....	vii

List of Figures

Figure 1:Flow diagram of highlighting steps in textile processing.....	7
Figure 2: Structure of direct black 22 dye.....	8
Figure 3: Ionization of direct black 22 dye in water	8
Figure 4: Crushed and sieved A) scoria and B) pumice.....	16
Figure 5: Stock solution (the left side) and powder of direct black 22dye (the right side).....	17
Figure 6: Effect of contact time on direct black 22-dye removal by pumice and scoria (initial dye concentration 50 mg/L,pH =4 and 5, adsorbent dose 1.6g and 2g using pumice and scoria respectively)	25
Figure 7: Effect of pH on the dye anion removal by pumice and scoria (initial dye concentration 50mg/L, time = 90min and 120 min, adsorbent dose =1.6 and 2g for pumice and scoria respectively).....	27
Figure 8: Decolonization before and after (A=before B= after agitated and centrifuged using pumice and C=after agitated and centrifuged using scoria but not filtered)	27
Figure 9 : Decolonization with different pH after agitated, centrifuged and filtered ready to read by spectrophotometry	28
Figure 10:Effect of concentration on direct black 22 onto pumice and scoria(time=90min and 120min,adsorbent dose 1.6g and 2g using pumice and scoria respectively).	29
Figure 11: Effect of dose on the dye anion removal by pumice and scoria (time =90min and 120min, pH =4 and 5, initial dye concentration 50mg/L for pumice and scoria respectively .	30
Figure 12: Effect of agitation time for direct black 22 50mg/L at 200 rpm using pumice and scoria	31
Figure 13: Langmuir non-linear isotherm model of adsorption of direct black 22 dye onto pumice and scoria.....	33
Figure 14: Freundlich non-linear isotherm model of adsorption of direct black 22dyes onto pumice and scoria.....	34
Figure 15: Plot of adsorption pseudo first order kinetics of direct black 22dyes onto pumice and scoria ($R^2= 0.71$ and 0.81 using pumice and scoria respectively).....	36

Figure 16: Linear pseudo second order kinetics for the adsorption of direct black 22 dye with initial concentrations 10,20,40 mg/L to adsorbent doses 0.8,1.6, and 3.2g respectively and (pH=4 and 5,time 90 min and 120 min using pumice and scoria respectively)..... 37

Figure 17: The average linear pseudo second order representation of direct black 22dyes onto pumice and scoria..... 38

Figure 18: Plot of qt vs $t^{1/2}$ ($R^2 = 0.83$ using pumice) 39

Figure 19: Plot of qt vs $t^{1/2}$ ($R^2 = 0.86$ using scoria) 40

Figure 20: Experimental procedure to determine the major interfering anions of direct black 22 dye 40

Figure 21: Effects of co-existing anions on adsorption of direct black 22dyes using pumice and scoria 41

Figure 22: Dose vs percentage removal efficiency of direct black 22 dye in real sample at (pH =6.4, concentration of dye 62.2mg/L, time =90min and 120 min using pumice and scoria respectively) 42

List of Tables

Table 1: Table some properties of direct black 22 dye	8
Table 2: Elemental composition and oxide content of red scoria and pumice XRF result	16
Table 3 : Langmuir non-linear isotherm equations and parameter	34
Table 4 : Freundlich non-linear isotherm equations and parameter.....	35
Table 5: Linear pseudo second order equations and related parameters.....	38
Table 6: Physicochemical characteristics Textile wastewater (Ayka Addis)	43
Table 7: Comparison of different adsorbents and different dyes with direct black 22	44
Table 8: Data of contact time	vii
Table 9: Data of effect of pH	vii
Table 10: Effect of initial concentration of direct black 22 dye	viii
Table 11: Data of effect dose of adsorbent	viii
Table 12: Data of Effect of agitation time	ix
Table 13: Desorption data	ix
Table 14: Data for Langmuir and Freundlich models (for both linear and non-linear)	ix
Table 15 : Data of pseudo first order	x
Table 16: Data of pseudo second order.....	x
Table 17: Data of intra-particle diffusion.....	xi
Table 18: Data of real sample (Co= 62.2 mg/L)	xi
Table 19: Data of effect of interfering Anions.....	xii

Abstract

A textile industry releases large amounts of dyeing chemicals, which create severe water pollution when discharged untreated. Most of these dyes, because of their carcinogenic and mutagenic properties, they threaten human health and aquatic life. Adsorptive-based experiment was employed to investigate direct black 22-dye removal capacity of pumice and scoria from aqueous solution and textile wastewater.

Preliminary test were conducted to optimize parameters. Optimum parameters of pH 4 and 5, adsorbent dose of 1.6g and 2g, contact time 90 min and 120 minutes, agitation time 30 min at shaking speed of 200 rpm and room temperature (22 ± 1) were used to investigate the adsorption capacity using pumice and scoria respectively.

Results of the study revealed that 50 mg/L direct black 22 dye ion concentrations reduced to 2.45mg/L and 3.1mg/L from aqueous solutions using pumice and scoria respectively. When compared to Nitrate and Fluoride, Phosphate, sulfate and chloride anions were the dominant interfering anions to compete direct black 22-dye tested in synthetic sample. Chloride was the dominant anion (973mg/L) found in wastewater analyzed for the experiment.

The equilibrium data best fit to Langmuir and Freundlich adsorption isotherm with a maximum adsorption capacity of 7.71mg/g and 8.1 mg/g with correlation coefficient R^2 (0.995 and 0.9899) using pumice and scoria respectively.

Direct black 22 dye uptake model well fitted with pseudo-second order with correlation coefficient R^2 (0.988 and 0.993) using pumice and scoria respectively.

The results of the study demonstrate that naturally available pumice and scoria can remove direct black 22 dyes from aqueous solution and it is better to remove the major interfering anions and mixture of cofactors with suitable pretreatment techniques for real or wastewater sample before adsorption to reduce the interfering ions competing with direct black 22 dye.

Key words: Direct black 22 dye, pumice and scoria, adsorption, adsorption capacity, interfering ions adsorption isotherms and adsorption kinetics

CHAPTER ONE

1. INTRODUCTION

1.1 Background of the study

The pollution of water as the result of industrial activities has been considered one of the major environmental issues in the world, especially in developing countries. The discharge of pollutants into water bodies by different activities like industries, as a global environmental problem, has been attracted worldwide attention because of their harmful effects on the environment and as well as human health (Khaniabadi et al., 2017).

Many industries, such as the textile, leather, paper and plastics industries, are highly dye users. The textile industry is the first by quantity and quality of dyes used for the dyeing of various fiber types. In addition to color of dyes, wastewater from the textile industry contains a number of other polluting matters, such as toxic organic residuals, acids, bases and inorganic matter. Some dyes particularly azo dyes are carcinogenic and mutagenic being formerly produced from dangerous chemicals, such as benzidine, metals (Kravić et al., 2010).

Textile industry consumes great amount of water and colored dyes, which generate high volume colorful wastewater. Approximately 1000 ton/yr of colored textile dyes are discharged into the effluents by textile industries in the world (Balarak, Pirdadeh and Mahdavi, 2015b). The effluence of textile colored liquid waste into receptor waters affects not only their esthetic nature but also disturbing natural balance of water life and the food chain. About 10-15% of synthetic dyes are lost during different process in textile industry to surface water in the world (Hassaan and Nemr, 2017).

In dyeing processes, plentiful of the color dye is lost in the wastewater. This can lead to acute effects on exposed organisms due to the toxicity of the dyes, abnormal coloration and reduction in photosynthesis because of the absorbance of light that enters the water (Habte, Zewge and Redi, 2014).

Major problems associated with colored effluent are lowering sun light penetration, photosynthesis and damages the aesthetic nature of the water surface. Moreover, their degradation products may be mutagenic and carcinogenic. Many dyes may cause allergic dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive and central nervous system (Mohammed, Shitu and Ibrahim, 2014).

A very small amount of dye anion in water (10-50 mg/L) is highly visible and reduces light penetration in water systems, thus causing a negative effect on photosynthesis (Lavanya, 2014).

Among dyes, over 50% of the total world production is azo dyes, owing to their low cost, variety, solubility and stability; they are characterized by an azo bond (-N=N-). Most azo dyes contain only one azo group, but some contain two (diazo), three (triazole) or polyazo (Samarghandiet al., 2013).

Azo dyes are toxic only after reduction and cleavage of the azo linkage to give aromatic amines, mostly via intestinal anaerobic bacteria. The aromatic amines groups are metabolically oxidized (NPTEL - National Programme on Technology Enhanced Learning, 2014).

Most of developing countries has resulted in the discharged of partially treated or raw wastes into the surrounding water bodies since the development of treatment facilities has not kept well with the rate at which the wastes are generated by the industries. For example Nigeria cities like Kaduna, Lagos, Kano and Aba depend very much on their rivers for water supplies (Berger and Bhowan, 2011).

In Ethiopia, textile production becomes the source of income that contributes to their gross domestic product. However, this has brought both consequences to such countries either in a positive way that is an improvement of economy or in a negative way which led to an increased anthropogenic impact on the biosphere (Desta, 2013).

Bahirdar textile factory possess serious pollution to aquatic habitat of the head of Blue Nile River in turn makes the water highly polluted (Mehari, Gebremedhin and Ayele, 2015).

In Addis Ababa, there are many industrial establishments among which most of them are discharging their effluents directly to river without any prior treatment (Tegegn, 2012).

Ayka Addis textile factory discharges its wastewater without proper treatment except addition of sulfuric acid to reduce its pH and urea to balance the fertility of the contaminated soil; due to this the dyes are polluting the environment (Soresa, 2011). Thus, the result of this study may find low cost remediation for dye removal for textile industry.

1.2 Statement of the problem

Residual textile dye is a problem because, in dyeing processes, as much as 50% of the dye color is lost in the wastewater. These losses are due to the relatively low levels of dye-fiber

fixation and the presence of un-reacted hydrolyzed dye color in the bath. Dye hydrolysis occurs when the dye molecule reacts with water. Therefore, residual reactive hydrolyzed dyes remain in the wastewater. These problems are due to the high water solubility of the dye and characteristic brightness of the dyes (Worku and Sahu, 2014).

Organic dyes are major pollutants which generally create pollution in the ecosystems and they are difficult to treat because of their different and complicated molecular structures (Ashtaputrey and Ashtaputrey, 2016). Many of the synthetic dyes particularly azo dyes are found to be carcinogenic and harmful to health and environment (Kechi, Chavan and Moeckel, 2013). Nitrogen and phosphorus in the dyes can contribute to stream eutrophication, and harmful to aquatic life if released (Petzoldt, 2014).

Human studies show that azo dyes can be reduced to aromatic amines by intestinal flora, which may be a cause for the connection between intestinal cancer and economic development, as developed countries typically consume more processed food, which may be colored with azo dyes. Thus, even if the dye itself is not toxic, it may break down into harmful products (Petzoldt, 2014).

Poly azo dyes have greater toxicity than mono or diazo dyes (Chequer, Dorta and Oliveira, 2011). The toxicity of aromatic compounds depends up on its substitution and numbers of azo groups attached to the ring. A direct black 22 dye is an azo dye with four or tetra azo dye with (-N=N-) bonded to the ring, therefore it is one of the toxic dye when it break down to its anionic (Mohammad and Azeez, 2005).

Even though the cost material of activated carbon is high, still many industries use it as adsorbents. However, taking into account the high costs involved in the preparation and regeneration process, the feasibility of alternate adsorbents has been studied recently by scientists. Therefore, other attempts that explore cheap, locally available and effective materials need to be made. A lot of commercially available, low cost which are used to remove dye from aqueous and wastewater. Therefore, the new adsorbents that are more economical, easily available and highly effective are still needed to mitigate the impact of dye from industries. Pumice and scoria are found in abundance in the world. So, it can be seen as a possible source of adsorbent for adsorption columns of industries (Parashar, 2012).

Pumice and Scoria are abundant in many places in the world including Central America, Southeast Asia (Vietnam, etc.), East Africa (Ethiopia, Kenya, etc.), and Europe (Greece, Italy,

Spain, Turkey, etc.) (Birhanie, Leta and Khan, 2017). Pumice and scoria, volcanic rocks, are highly abundant around rift valley of our country, Ethiopia. Pumice is a light porous igneous volcanic rock with large surface area and has high water adsorption capacity (Asere, Mincke, Clercq, et al., 2017). Thus, looking for materials for efficient removal of dyes from wastewater is very important and this study investigated adsorptive removal of direct black 22-dye anion from aqueous solution and from wastewater onto pumice and scoria. Thus, the aim of this work is to evaluate removal efficiency of pumice and scoria as an alternative adsorbent for the removal of direct black 22 dye from aqueous solution and wastewater.

1.3. Significance of the study

Adsorption technology has major importance in mitigating environmental pollution for it is low cost, locally availability, environmentally friendly, easy operation and handling, small sludge, high removal efficiency due to large surface area, without additional nutrient requirement.

The study is used to test the adsorption efficiency of dye from aqueous solution and wastewater by using pumice and scoria. Therefore, the outcome of this study would help to mitigate the effect of dye on environment and health of people living around downstream of the river where the wastewater Ayka Addis textile is discharged.

The result of this study would also help to mitigate the impact of dye in general and azo dye in particular from textile industries on public health and environment through reducing the amount of dyes discharged to nearby surface water by adsorption to pumice and scoria. As a result, the treated water may be used for recreation, toilet flushing, and reuse for industrial processing and become conducive for aquatic life.

Moreover, the outcome of this study gives insight for the Ethiopian environmental authority for effluent discharge limit of dyes/azo dyes. As adsorptive capacity of pumice and scoria needs optimization, this study would be used as baseline for further research.

1.4. Research questions

- What is the adsorptive removal efficiency of direct black 22 dye using pumice and scoria?
- What are the factors that influence the adsorptive removal efficiency of direct black 22 dye using pumice and scoria?
- Which adsorption isotherm model for experimental data to which the model fits?
- Which kinetic model best fit the experimental data?
- Which adsorbent is more efficient for the removal of direct black 22dyes?
- What are the major anions that interfere the removal of direct black 22 dye?

CHAPTER TWO

2. LITERATURE REVIEW

2.1 History of synthetic dyes

The textile dyeing industry has been in existence for more than 4,000 years ago. For the last 150 years, the dyes were obtained from natural sources. Nowadays bright, fast, inexpensive synthetic are available. During the early Roman Empire period, only kings and priests could wear purple dyed fabrics while in the Middle Ages, scarlet dyed fabrics were reserved exclusively for important members of the clergy. Dye sources were even important enough to lend their names to new world countries. Thus, the similarity between ‘Brazil wood’ from indigenous Indo-Asian caesalpinia trees and vast numbers of a related species growing in the South American region originally called ‘Terra de Vera Cruz’ led Spanish explorers to rename the country ‘Brazil’ (Ferreira, Hulme and Quye, 2004).

The first known use of an organic colorant was much later, 4000 years ago, when the blue dye indigo was found in the wrappings of mummies in Egyptian tombs. These dyes are commonly used in a number of industries, such as textiles, food, cosmetics and paper printing, with the textile industry the prominent consumer of dyes (Benkhaya, Harfi and Harfi, 2018).

2.2. Processing steps in a textile industry

Wet processing includes pretreatment, dyeing, printing and finishing. This process are carried in aqueous medium (Moutinho, Bertges and Assis, 2007).

Sizing is done to remove the loose hairy fibers from the surface of the cloth, to get smooth, even and clean looking face

Desiring is the process to remove sizing materials from the fabric, which is used to increase the strength of the yarn.

Scouring is a chemical washing to remove natural wax and non-fibrous impurities (e.g. the remains of seed fragments) from the fibers and any added soiling or dirt.

Natural coloration and the remaining impurities is bleached by NaOH and H₂O₂. These are oxidizing agent.

Mercerizing is a treatment for cotton fabric and thread that gives fabric or yarn a lustrous Mercerizing of fabric and yarn is carried out to get appearance and strength. This is done by treating with NaOH. The temperature and time are the two controlling factors in this process.

In finishing, all bleached, dyed, printed and certain grey fabrics are subjected before sending to the market and get good fit for their purpose.

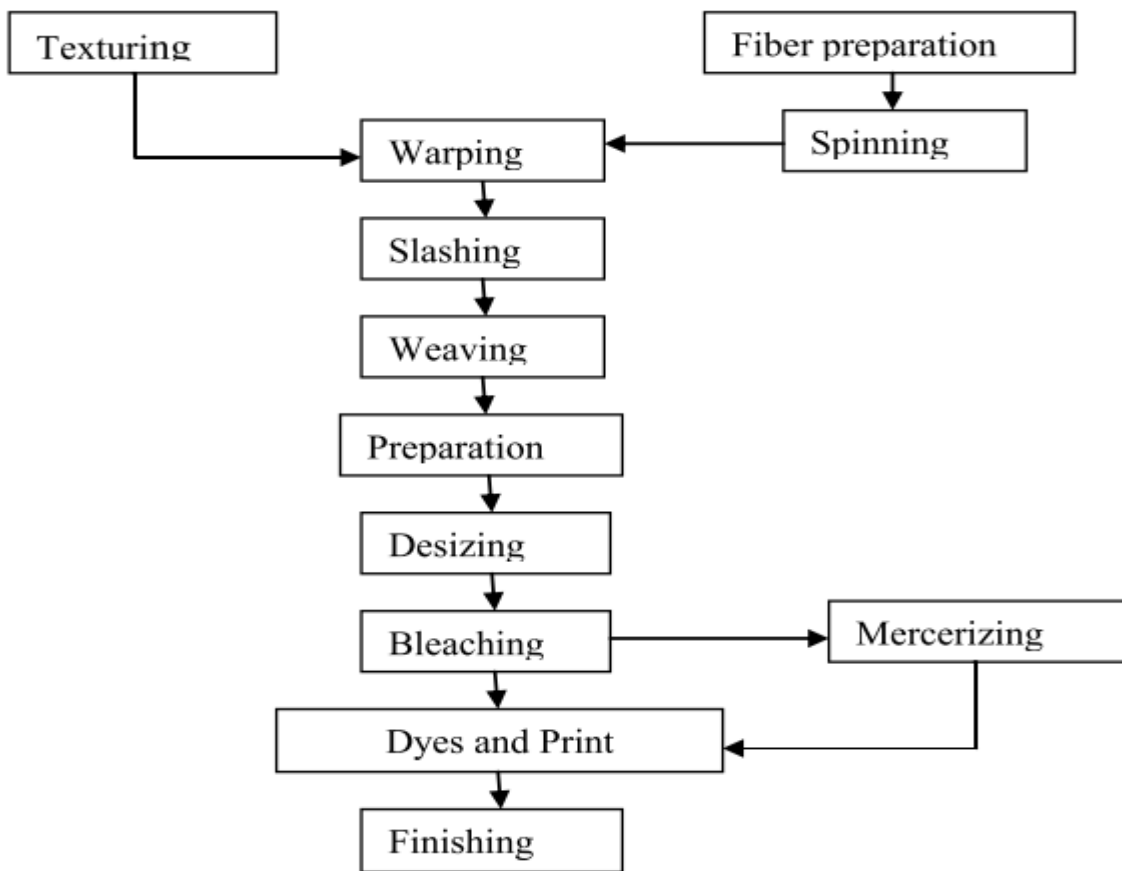


Figure 1:Flow diagram of highlighting steps in textile processing(Moutinho, Bertges and Assis, 2007)

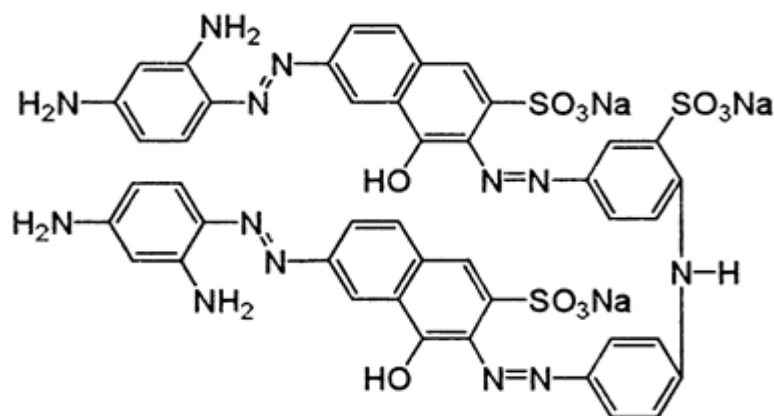
2.3. Chemistry of dye

Unlike most organic compounds, dyes possess colour because they a) absorb light in the visible spectrum(400–700 nm), b) have at least one chromosphere (colour-bearing group), c) have a conjugated system, i.e. a configuration with alternating double and single bonds, and d) exhibit resonance of electrons. In addition to chromospheres, most dyes also contain groups

known as auxochromes (colour helpers), examples of which are carboxylic acid, sulfonic acid, amino, and hydroxyl groups('General introduction to the chemistry of dyes', 2010).

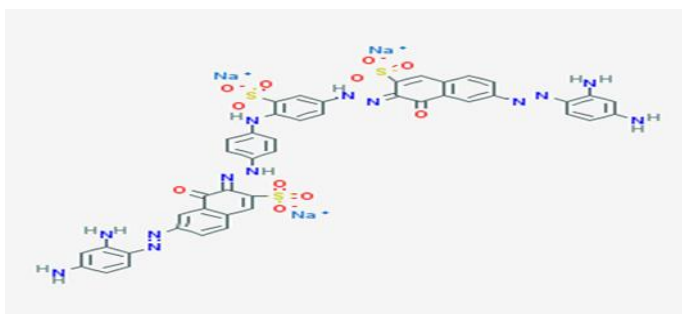
Table 1: Table some properties of direct black 22 dye

Name of dye	Formula	M.Wt	λ_{max}	Chromophore dye
Direct black 22	$C_{44}H_{32}N_{13}O_{11}S_3Na_3$	1083	484	Polyazo



www.worlddyevariety.com>directdyes

Figure 2: Structure of direct black 22 dye



https://pubchem.ncbi.nlm.nih.gov/compound/Direct_black_22

Figure 3: Ionization of direct black 22 dye in water

2.4. Sources of dye Contaminations

Dye and dye intermediates industries, pharmaceutical industries, tannery, and Kraft bleaching industries etc) discharge different variety of organic pollutants into natural water resources or wastewater treatment systems. One of the main sources with major pollution problems worldwide is the textile industry. Its dye-containing wastewaters (i.e. 10,000 different textile dyes with an estimated annual production of 7.10^5 metric tonnes are commercially available worldwide. Nearly 10-25% of textile dyes are lost during the dyeing process, and nearly 2-20% are directly discharged as aqueous effluents in different environmental components (Carmen and Daniela, 2010). Textile industry and its finishing products has created a huge pollution problem. Textile industry is one of the most chemically intensive industry and which can pollute clean water. Many of the chemicals are poisonous and damaging to human health, aquatic life and the environment. Textile factory require a huge quantity of water for processing and dyeing. Daily water consumption textile having a production of about 8000 kg of fabric per day is about 1.6 million liters in average. Of this, 16% consumed in dyeing and 8% in printing (Bhatt and Rani, 2013).

2.5. Types of dye

Dye can be classified by their solubility in water or else by their particle charge during dissolution such as anionic dyes (reactive, direct and acid dye), cationic dye (basic dye) and also non-ionic dye (disperse dye). In addition, anionic and cationic dye including in water soluble dye while non-ionic dye is in the categories of water insoluble dye. Reactive dye been design for cellulose fiber and contain high colour of organic substance. This reactive dye has high solubility in water and the most permanent dye among others dye. There are different types of direct dyes. Direct textile dyes (direct red 81, direct blue 15, direct black 22 and direct orange 34 etc). Some azo direct dye may contain benzidine based dye that could result an exposure to allergies, irritation, cancer risk and treating aquatic life if they are directly release without any treatment (Mohammad Razi, Mohd Hishammudin and Hamdan, 2017).

2.6. Toxicity of dye and mobility in the environment

The possible long-term effects of a few dyes particularly azo dyes and their degradation products are becoming increasing concern to human health. Mutagenic, carcinogenic and/or allergenic effects of dyes have been studied. About 90% of some 4000 different dyes tested, LD50 (Lethal Dose at 50% survival) values greater than 2×10^3 mg/kg. The highest rates of toxicity were found amongst azo dyes (Joshi, Bansal and Purwar, 2004).

In addition to their toxic dye anion, synthetic dyes when they are ejected into the wastewater the aqueous modify water chemistry, changing the pH of the solution, the color, chemical oxygen demand that hinders the growth of microbial organisms. Under the action of microorganisms, dyes release of nitrates and phosphates in the environment, these ions can become toxic to fish life and alter the production of drinking water; consumption by the aquatic plants accelerated their uncontrolled growth and leads to oxygen depletion by inhibiting photosynthesis. The species found at the top of the food chain, including man finds himself exposed to toxic levels of a bioaccumulation even at the base of low concentration that we had (Ouezzani, Hourch and Azzouzi, 2016).

While dye–substrate affinity is critical, synthetic dyes cannot be commercialized unless they pose little health risk under end-use conditions. Consequently, environmental safety is an essential consideration in molecular design. It is clear, therefore, that dye design must take into consideration for toxicity of the environment and metabolites in mammalian systems ('General introduction to the chemistry of dyes', 2010).

2.7. Dye removal technologies

There are various ways to remove dyes from wastewater discharges like coagulation, adsorption electrochemical process, membrane separation process, chemical oxidation, reverse osmosis and aerobic and anaerobic microbial degradation. Considering their economic disadvantages and inefficiency, many of these processes are not popular. Coagulations and chemical and electrochemical oxidations have low feasibility on large-scale treatment plants.

Adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface. The famous process that been studied by researchers is adsorption. Organic dye, toxic chemical, phenol, pesticides, colour, soluble organic pollutants and cyanides are effectively removed by adsorption. Low cost, easy operation, flexibility and simplicity

makes adsorption process preferred over other processes. It occurs in three-step process:-the adsorbate diffuses from fluid stream to the external surface of adsorbent, the adsorbate shifts to the pores of the adsorbent particles and the molecules adhere to the surface area of pores. Most of adsorption occurs in these pores because of their large surface area (Parashar, 2012).

2.7.1. Types of adsorption

Depending on the type of attractions between adsorbate and adsorbent it can be physical adsorption (attracted by weak van der Waals) and chemical adsorption (of and chemical adsorption (Panić et al., 2013).

2.7.1.1. Physical adsorption

It is a type of adsorption in which molecules are attracted by weak van der Waals forces and forming multi-molecular layers on the layer of adsorbents (Berger et al, 2011).

2.7.1.2. Chemisorption

It is a type of adsorption in which molecules adheres to the surfaces of adsorbent by forming a covalent chemical bond. It forms monolayer on the surface of adsorbents. It forms stronger bond than physical adsorption (Berger et al., 2011).

2.8. Properties of Pumice and scoria

Pumice and scoria, volcanic rocks, are abundant in many parts of the world. They are the result of volcanic ash. They have been used for a long period for construction purposes in the world with vesicular glassy lava of basaltic andesitic with the composition of SiO_2 . The vesicular structure and chemical properties of pumice and scoria have different useful properties such as low bulky density, good thermal, caustic insulation, low chemical reactivity and very porous (Ali, 2013). Pumice is a light porous igneous volcanic rock with large surface area and high water adsorption capacity (20-30%), whereas scoria is formed of vesicular fine to coarse fragments, reddish or black color, and light size (Asere et al., 2017).

2.9. Characterization of adsorbents

As seen in Table1, the main component of the adsorbent was SiO_2 (62.2%) and (42.2%) for pumice and scoria respectively. Other elements except K (3.9%) in pumice and Ca (6.3%) in scoria were present in relatively smaller amounts. From the Scanning Electron Microscope

(SEM) image specific surface area of pumice and scoria were 3.88 and 2.63 m²/g respectively (Asere *et al.*, 2017)

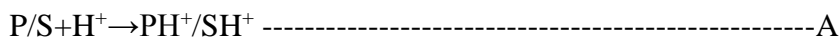
The Fourier-Transform Infrared Spectroscopy (FTIR) result of pumice at wave numbers (\approx 1055, 3626 and 2941cm⁻¹) with their corresponding functional groups represents were Si–O–Si, Al–Al–OH and H–O and C–H respectively (Yapar, 2015). For scoria the FTIR at wave numbers (\approx 1620, 1070, 2900 and 3600 cm⁻¹) with their corresponding functional groups, it represents OH, Si–O and Al–O, C-H and Si–O–Al respectively (Moradi *et al.*, 2015).

2.10. Effect of pH solution and adsorption mechanism of pumice and scoria

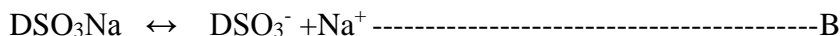
Adsorbent surface charges play a significant role in adsorption process (Zarrabi, 2012a).

In order see the adsorption mechanism between the surface of adsorbent and anions of direct black 22 dye, it is better to consider the following equations:-

In aqueous solution and at low pH, the surfaces of the adsorbents are protonated forming positive charge on the surface. Let us say P and S represent pumice and scoria surfaces respectively and then equation ‘A’ and ‘B’ shows the above fact as follows:-



In aqueous solution direct black 22 dye first dissolved and then decomposed to the corresponding anionic dye group as follows:-



(Where DSO₃⁻ represent the complex anionic dye and then equation ‘B’ shows dissociation of the direct black 22 dye in aqueous solution.

In Eq. (A) and Eq. (B), the adsorption process continues due to electro-static interaction between the two counter-ions DSO₃⁻ and P⁺/S⁺ (Eq C).



At pH greater than 7 the surfaces become anionic (OH⁻) and the dye anion DSO₃⁻ competes for the site.

From the above equation, the sorption capacity of pumice and scoria in acidic conditions would increase. Therefore, acidic conditions leading to increasing amount of protons or H⁺ ions, at the surface of pumice and scoria, consequently improve dye removal .The same reaction can be transposed to other compounds of pumice and scoria such as SiO₂, Al₂O₃, CaO, FeO and MgO(Heibati, Rodriguez-couto, et al., 2014)

2.11. Adsorption process

Mixing various adsorbent doses (0.5-2.5 g) (Zarei, Pezhhanfar and Someh, 2017) to 100ml of stock synthetic solution, while maintaining the others parameters constant. Different pH ranges (2-12) (Khaniabadi *et al.*, 2017). The pH investigation was carried out to determine the optimum pH at which maximum dye ion adsorption was revealed by pumice and scoria. The changes of absorbance were determined at certain time intervals (5-120min) (Shoair and Mohamed, 2015) during the adsorption process while, varying initial dye concentrations (5-300 mg/L) (Habte, Zewge and Redi, 2014). The ion solution agitation time interval (5-90) at 200 rpm, centrifuged at 4000rpm and room temperature ($22\pm 1^{\circ}\text{C}$) for 1hrs (Heibati, Rodriguez-Couto, et al., 2014). Afterwards, the solid was separated by filtration using Whatman No.1 filter paper (Abdus-salam et al., 2014).

CHAPTER THREE

3. OBJECTIVE

3.1 General Objective

- ❖ The general objective of this study is to investigate direct black 22 dye removal capacities of pumice and scoria from aqueous solution and wastewater.

3.2 Specific Objective

- ✓ To determine dye removal efficiency using pumice and Scoria
- ✓ To evaluate the effect of contact time, pH, adsorbent dose, initial concentration of direct black 22 dye and agitation time.
- ✓ To investigate an experimental data fitness among adsorption isotherm and kinetics.
- ✓ To evaluate interfering anions on direct black 22 dye removal efficiency

CHAPTER FOUR

4. MATERIALS AND METHODOLOGY

4.1. Study Design

Laboratory based experimental study design was carried out to determine the efficiency of pumice and scoria as adsorbent on removal of direct black 22 dye in aqueous solution and wastewater of textile industry. Batch adsorption mode was carried out.

4.2. Study variables

Independent variables are: pH, contact time, initial dye concentration, agitating speed, co-existing ions, adsorbent doses, equilibrium time, regeneration process, adsorption isotherms and adsorption kinetics of the adsorbent was studied.

Dependent variables:-adsorptive capacity of Pumice and scoria

4.3. Instrument and Apparatus

Multi-parameter probe (HQ40d), pH meter, UV- Vis spectrophotometer (Model DR 5000), different sized volumetric flasks, mortar and pestle, beakers, measuring cylinders, drying oven (GTF binder, Germany), filter funnel, conical flask, graduated cylinder, Shaker (Model EdnurdhuhlarGmbH, SM-30) Sieve (<1-3mm), polyethylene container flasks, whatmanno.42 filter paper, analytical balance, were used during the experiment.

4.4. Chemicals

The chemicals used for this study includes direct black 22dye obtained from Ayka Addis textile factory, and sodium hydroxide 0.1N, hydrochloric acid 0.1N for pH adjustment (Samarghandi *et al.*, 2013). All chemicals used in this study were analytical reagent grade. The chemicals used for interfering ions were salts of NaNO_3 , CaF_2 , NaNO_3 , NaHCO_3 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, NaCl , $(\text{NH}_4)_3\text{PO}_4$ and MgSO_4 .

Table 2: Elemental composition and oxide content of red scoria and pumice (Asere et al., 2017) XRF result

Elements	Pumice % (wt)	Red Scoria % (wt)	Oxides	Pumice % (wt)	Red Scoria % (wt)
Si	27.3	18.4	SiO ₂	69.2	42.2
Al	5.6	9.7	Al ₂ O ₃	11.9	18.4
Fe	3.3	8.1	FeO	5.8	13.0
K	3.9	0.3	CaO	0.9	11.1
Ca	0.2	6.3	K ₂ O	6.3	0.6
Na	1.0	2.3	Na ₂ O	1.6	3.4
Mn	<0.1	0.1	CuO	1.7	1.6
Mg	<0.1	2.2	ZnO	1.3	1.3
Zn	<0.1	<0.1	NiO	1.0	1.9
Cr	<0.1	<0.1	MnO	0.1	0.2
Cu	<0.1	<0.1	MgO		4.1
Co	<0.1	<0.1	TiO ₂		2.3
Cd	<0.1	<0.1			
Ni	<0.1	<0.1			
Pb	<0.1	<0.1			
As	<0.1	<0.1			

4.5. Adsorbent collection and preparation

The Adsorbents were collected from Rift valley area of Oromia National Regional State Ethiopia, East of Addis Ababa around Adama. It was transported to Jimma University Environmental health science and technology for laboratory analysis. They were dried at 103⁰C for 6 hours. Finally, it was crushed and sieved to 1-3mm and used as adsorbent (Asadi *et al.*, 2016).



Figure 4: Crushed and sieved A) scoria and B) pumice

4.6. Preparation of dye solution

An accurately weighted 1gm of the dye was dissolved in 1000ml of distilled water to prepare stock solution (1000mg/L). The pH of each experimental observation was maintained with the use of 0.1N HCl or 0.1N NaOH.



Figure 5: Stock solution (the left side) and powder of direct black 22 dye (the right side)

4.7. Collection of real sample solution

The actual wastewater was collected from Ayka Addis textile factory Addis Ababa, Ethiopia. Time-related composites, which are made up of sub samples of equal volume taken at 3hr time intervals (morning (9: 00AM), midday (6:00AM) and afternoon (9:00PM) was used. The wastewater was taken from four different places after treatment from its effluent and from the outlet of the dyeing machine before it is treated to know initial concentration. The volume of wastewater taken was 6L and it was transported to Jimma University Environmental Health Science and Technology laboratory with plastic bottle rinsed with 0.1HCl. The physicochemical was determined according to standard method analysis (APHA, 2012).The dye liquor pH and total dye concentration was measured before application with adsorbent. Then this sample was subjected for extraction of dye using the sorbent developed at optimum conditions of pH, equilibrium time and sorbent.

4.8. Adsorption Procedures of synthetic dye

After the experiments conducted in laboratory (agitation, centrifugation and filtration), dye ion concentration in the supernatant was determined by spectrophotometer (at λ_{\max} 484 nm) (NidalZa'tar et al., 2005). The averages of triplicated measurements were reported.

4.8.1. Determination of Adsorption Efficiency

Batch mode adsorption studies for individual parameters were carried out using 250 ml Erlenmeyer flask. The effects of different parameters such as concentration of direct black 22 dye, adsorbent dose, contact time, agitation time and pH were studied. Standard solutions of the dye were mixed with the adsorbent and agitated at 200rpm on mechanical shaker for 30 min. Finally, the resulting suspension of each of the dye was filtered using a whatman No.1 filter paper and the filtrate was analyzed for the corresponding dye concentration by spectrophotometer. Removal efficiency was finally calculated by using the following relationship: -

The amount of dye ion adsorbed at time t, q_t (mg/g) was calculated by the following expression:

$$q_t = (C_0 - C_t) \frac{V}{m} \text{-----} (1)$$

Where C_0 and C_t (mg/L) stands for the concentration at initial and time t. V (L) is the volume of solution, and m (g) is the mass of sorbent used (Ma et al,2014)

And also the percentage of dye adsorption (removal) was calculated by the expression;

$$A\% = \frac{C_i - C_e}{C_i} * 100 \text{-----} (2)$$

Where, C_i and C_e are initial and final equilibrium dye concentrations (mg/L) respectively. A is the percentage of dye adsorbed (Khaniabadi *et al.*, 2017).

4.8.2. Effect of Contact Time

The effect of contact time was investigated by varying contact time from 5 to 210 min. While, the dose = 1.6g and 2.0g for pumice and scoria respectively, direct black 22 dye concentration of 50mg/L pH = 4 and 5 were used for pumice and scoria respectively. The amount of the direct black 22 dye adsorbed per unit mass of the adsorbents media and the percentage adsorption was calculated by using equation 1 and 2 above.

4.8.3. Effect of pH solution

Varying pH solution from 3 to 10 while maintaining others parameters such as contact time 90 min and 120 min, dose 1.6g and 2g for pumice and scoria respectively. Initial direct black 22 dye concentration 50mg/L agitation speed 200 rpm at 30.

4.8.4. Effect Initial Concentration of direct black 22 dye

The effect of initial concentration of direct black 22-dyewas examined by varying the concentration of direct black 22 dye (5 to 250 mg/L)while maintaining the optimum pH of the solution, agitation speed, contact time and adsorbent dose.

4.8.5. Effect of Dose

The effect of adsorbent dose was investigated at the different adsorbent doses ranging from (0.4 to 2.8g). With optimum pH of the solution, agitation speed of 200 rpm, equilibrium time and initial direct black 22 dye 50 mg/L in 100 mL of the solution to determine the optimum dose required for the reduction of direct black 22-dye anion in water.

4.8.6. Effect of agitation time

A 50mg/L of the dye solution were measured into a 100 ml flask and contacted with 1.6g and 2g of the adsorbent at room temperature. The flasks were labeled for time difference of 5, 10, 15, 30, 45, 60 and 90 min. and flasks were tightly covered and agitated for the appropriate time using shaker 200rpm. At the end of the timing scheduled each of the flasks were brought out, centrifuged and suspensions were filtered using filter paper. The un-adsorbed dye was determined with UV/Vis spectrophotometer. The quantity adsorbed was calculated.

4.9. Adsorption isotherms

An adsorption isotherm is a graphical representation expressing the relation between the mass of dye adsorbed at constant temperature per unit mass of adsorbent and liquid phase dye concentration at equilibrium. It shows how dye can be distributed between the liquid and solid phases at various equilibrium concentrations. Langmuir and Freundlich isotherms were used to study adsorption mechanism and to determine maximum adsorption capacity of the adsorbents(Desta, 2013).

4.9.1. Langmuir isotherm

Langmuir isotherm is based on the assumption that the point of valance exists on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site would not affect the adsorption of molecules at an adjacent site(Langmuir, 1917; Zarrabi, 2012a).

The general linear equation:

$$C_e/q_e = (1/q_m b) + (1/q_m) C_e \dots\dots\dots (3)$$

C_e is the equilibrium concentration (mg/l) and q_e the amount adsorbed at equilibrium (mg/g).The Langmuir constants q_m (mg/g) represent the monolayer adsorption capacity and b (l/mg) relates the heat of adsorption (Banerjee and Chattopadhyaya, 2017).

In order to evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter;

$$R_L = \frac{1}{1+bC_o} \dots\dots\dots (4)$$

b (Lmg⁻¹) is the Langmuir isotherm constant and C_o (mg /L) is the initial concentration of dye. There are four probabilities for the R_L value: The adsorption process is irreversible if $R_L = 0$, favorable if $0 < R_L < 1$, linear if $R_L = 1$ and unfavorable if $R_L > 1$ (Langmuir, 1917; Zarrabi, 2012a).

4.9.2. Freundlich isotherm

Freundlich isotherm provides the detailed idea about the effectiveness of the adsorbent and the maximum amount of adsorbate would get adsorbed by the adsorbent. The Freundlich equation is basically empirical but it is often useful as a means for data description. It describes the heterogeneous surface energies by multilayer adsorption (Anirudhan and Ramachandran, 2015).

The general linear equation:

$$\log q_e = \log K_f + 1/n \log C_e \dots\dots\dots (5)$$

K_f indicates adsorption capacity (mg/g) and $1/n$ an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. For values in the range

$0.1 < 1/n < 1$, adsorption is favorable. The greater the values of K_f better is the favorability of adsorption.

The amount of dye ion adsorbed per unit mass of adsorbent was obtained using the equation:

$$q_e = (C_i - C_e) V/m \dots\dots\dots 6$$

Where

q_e is the mass of adsorbate (dye ion) adsorbed per unit mass of adsorbent (mg/g adsorbent)

C_i is the initial concentration (mg /L) of dye ion in solution

C_e is the final (equilibrium) concentration (mg/L) of dye ion in solution

V is the volume (L) and m is the mass of adsorbent (g) (Mupa, Rutsito and Musekiwa, 2016).

The non-linearized form of Langmuir and Freundlich isotherms are given in equation below respectively: -

$$q_e = q_{max} b C_e / (1 + b C_e) \dots\dots\dots (7)$$

$$q_e = K_f C_e^{1/n} \dots\dots\dots (8)$$

Where C_e (mg/L) is the dye concentration in the aqueous phase at equilibrium; q_e (mg/g) is the dye adsorption capacity at equilibrium; q_{max} (mg/g) is the maximum adsorption capacity based on the Langmuir equation; b (L/mg) is the Langmuir constant; K_f (mg/g) is the adsorption coefficient; $1/n$ is the adsorption intensity.

Besides the coefficient of determination, the nonlinear chi-squared (χ^2) statistic test was used to identify the best fit model to the observed experimental equilibrium isotherm data. χ^2 is computed using Equation:

$$\chi^2 = \sum (q_e - q_{e,cal})^2 / q_{e,cal} \dots\dots\dots (9)$$

Where $q_{e,cal}$ (mg/g) is the equilibrium capacity calculated from the model; and q_e (mg/g) is the experimental equilibrium capacity. A small χ^2 value indicates similarity between the modeled and the experimental data, whereas a larger χ^2 value implies variation between the modeled and experimental data (Asere, Mincke, Clercq, et al., 2017)

4.10. Adsorption kinetics

To evaluate the kinetic parameters, Pseudo first order, Pseudo second order and intra particle were implemented to analyze the experimental data (Habila *et al.*, 2014). Initial direct black 22 dye concentration of 10 mg/L, 20mg/L and 40mg/L with adsorbent dose of 0.8g, 1.6g and 2g respectively was subjected to under similar conditions to study the adsorption kinetics (Johnson, 2014).

4.10.1. Pseudo first order kinetics

The pseudo first-order rate expression is:

$$\text{Log}(q_e - qt) = \text{log } q_e - (K_1/2.303) t \dots\dots\dots (10)$$

Linear plots of $\text{log}(q_e - qt)$ versus t indicate the applicability of this model (Alebachew and Yadav, 2017)

4.10.2. Pseudo second order kinetics

The pseudo second-order rate expression is:

$$t/qt = 1/K_2 q_e^2 + t/q_e \dots\dots\dots (11)$$

If the pseudo second-order kinetics is applicable, the plot of t/qt versus t should give a linear relationship (Balarak, Pirdadeh and Mahdavi, 2015b)

4.10.3 Intra-particle Diffusion

Despite the fact, adsorption is a surface phenomenon; the adsorbate may also diffuse into the interior pores of the adsorbent, which may influence the rate of reaction.

$$q_e = k_3 t^{1/2} + C \dots\dots\dots (12)$$

Where k_3 ($\text{mg/g}\cdot\text{min}^{-1/2}$) is the intra-particle diffusion rate constant and C (mg/g) is the intercept. If the rate-limiting step of dye removal is the intra-particle diffusion, the plot of q_e against the $t^{1/2}$ should be a straight line and pass through the origin (Worku and Sahu, 2014).

4.11. Adsorption of interfering anions and real sample

The competing anions chosen for study were the common anions present in natural waters, sulfate, nitrate, chloride, phosphate, fluorides, and carbonate. The synthetic mixtures of dye and one of the interfering anions was prepared. A stock synthetic solution having dye concentration of 50mg/L was prepared in distilled water. The influence of interfering anions on the removal efficiency was examined using each anion separately and in a mixture. 100 ml of these solutions was taken in stopped bottles and then correctly weighed optimum quantities of the promising sorbents (1.6 using pumice and 2g using scoria) were added. Optimum pH was adjusted to pH 4 and 5, time 90min and 120 min using pumice, and scoria respectively with 0.1N of HCl or NaOH. The samples were shaken in shaking machines. Then the samples were filtered, analyzed for dye and percentage of extraction was calculated from the data obtained.

For real adsorption, the adsorption experiment for direct black 22 dye ion from wastewater on to pumice and scoria was investigated triplicating without adjusting the pH of the wastewater. The dose of adsorbents (pumice and scoria) 0.4 to 2.8g with particle size of less than 1-3 mm using wastewater collected from textile effluent. Concentration of the wastewater collected was 62.2mg/L with pH of 6.2. The adsorption was conducted following the same adsorption procedure with the synthetic solution at optimum time of 90 min and 120 min for pumice and scoria respectively. Then this sample was subjected for extraction of dye using the adsorbent developed at optimum conditions, equilibrium time and then percentage of DB 22 removal was calculated (Asere, Mincke, De Clercq, *et al.*, 2017).

4.12. Desorption Studies

The residues (cake) on the filter paper was used for the desorption experiments. The What man filters used for the adsorption experiments were placed in bottles containing 100 mL distilled water and the mixture was agitated at 200 rpm at room temperature. The samples were filtered and the filtrate dye ion content was measured by spectrophotometer. The pH values of the solutions was measured with a pH-meter, before and after adsorption as well as after desorption experiments (Samarghandi *et al.*, 2013). Similarly, all the experiments were carried out in triplicate and the mean values were reported.

$$\% \text{Desorption} = \frac{C_e}{C_i} * 100 \text{-----} (13)$$

4.13. Statistical analysis

All experiments were measured in triplicate during the determination of direct black 22-dye concentration using UV- Visible Spectrophotometer. It was analyzed by averaging the values. The curve fittings of the data obtained were performed using Minitab16 and Microcal Origin 8.0 software and Microsoft excel 2010.

4.14. Quality Control

Triplicate experiments were carried out to avoid any discrepancy in results with the reproducibility and the relative deviation of the orders. Blank samples without ions were used as control and average data was reported. All chemicals used in this study were analytical reagent grade.

CHAPTER FIVE

5. RESULTS AND DISCUSSION

5.1. Effect of Contact Time

The effect of contact time was investigated by varying the time from 5 to 210 min under initial dye concentration of 50 mg/L, pH 4 and 5 and adsorbent dose of 1.6g and 2.0g for pumice and scoria respectively with agitation speed 200 rpm for 30 minutes at room temperature (22 ± 1) °C. The result of the experiment was presented in Figure 6 for both pumice and scoria. As seen in Figure 6, the highest rate of direct black 22 took place during 0-30 minute interval. In the remaining concentrations, this reduction continued up to 90 and 120 min with lower slope using pumice and scoria respectively.

The experimental result showed that a rapid rate of dye ion uptake during the first 30min contact time, reaching about 85.8% and 83.5% of dye ion removed for pumice and scoria respectively. The dye ion being removed within 30 minute is due to the greater concentration gradient and the availability of adsorption sites and the instantaneous utilization of the most readily available active sites on the outer surface of adsorbents by dye ions (Kebede et al., 2014).

This trend was reported for removal of methylene blue from aqueous solution using bio char prepared from Water Hyacinth-molasses (first 30 minute) (Mupa, Rutsito and Musekiwa, 2016). Anionic dye removal from aqueous solution (first 60 min) (Alexandrica et al., 2015). Removal of methylene blue by activated carbon (first 45 min) (Razi, Hishammudin and Hamdan, 2017) and Adsorption of acid red using dried lemna minor biomass (first 60 min) (Balarak, Pirdadeh and Mahdavi, 2015a). With an increase in contact time, slow adsorption was recorded until 210 min equilibrium time giving dye ion removal efficiency of about 96.6% and 95.8% for pumice and scoria at 90min and 120min respectively. This 90min and 120min was the saturation time at which maximum percentage removal was obtained for pumice and scoria respectively. Almost the same result was reported: removal of methylene blue by activated carbon (120min) (Mohammad Razi, Mohd Hishammudin and Hamdan, 2017). Adsorptive removal of hazardous azorhodanine dye from aqueous solution using rice straw fly ash (75 min) (Shoair and

Mohamed, 2015). Dyes removal from textile wastewater using orange peels (120 min)(Abdurrahman, Akter and Abedin, 2013). Removal of methylene blue from aqueous solution by mosambi fruit peel(120min)(Of *et al.*, 2016). Beyond this (i.e. 90min for pumice and 120 min for scoria), no significant increases of the dye adsorption which might be due to the presence of fewer adsorption sites and a lower dye concentration (Samarghandi *et al.*, 2013). Therefore, the contact time of 90 min and 120min was fixed for further studies for pumice and scoria respectively for direct black 22dye.

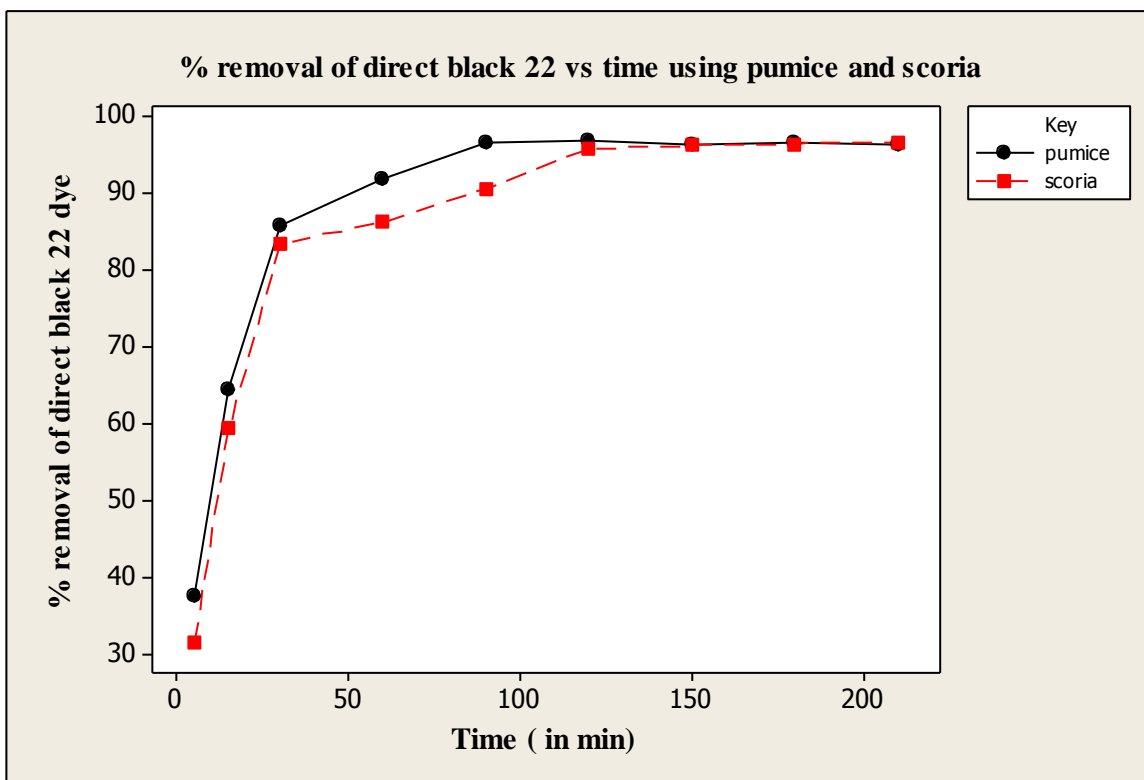


Figure 6: Effect of contact time on direct black 22-dye removal by pumice and scoria (initial dye concentration 50 mg/L, pH =4 and 5, adsorbent dose 1.6g and 2g using pumice and scoria respectively)

5.2. Effect of pH on adsorption mechanism

The pH of the solution has an important role in the adsorption process. Based on the result of pH, the surfaces of the adsorbents (pumice and scoria) are positively charged. As the pH of pumice and scoria were at lower values (pH 3, 4 and 5) removal efficiencies increases. When introduced into the solution, direct black 22 dye dissolved and formed negative

sulphonate groups. Due to the positive charge of pumice and scoria in acidic conditions, the surface charge increases) (Eqn i)



Therefore, acidic conditions leading to increasing amount of H⁺ ions, especially at the surface of adsorbents, consequently improve dye removal (Zarrabi, 2012a).

This phenomenon leads to high electrostatic attraction between the positively charged of adsorbents (pumice and scoria) and the negatively charged dyes, inducing therefore high removal of anionic dyes in acidic conditions, as it was experimentally confirmed by experiment and Figure 7 indicates the result for both pumice and scoria.

Indeed, a decrease of the removal for increasing pH was shown, from 96.3% at pH 4 to 57.1% at pH 10 for pumice and 94.6% at pH 5 to 60.2 % at pH 10 for scoria. The decrease in removal efficiency at pH greater than 7 can be attributed to the competition for the active sites by OH⁻ anions and the electrostatic repulsion of anionic dye by the negatively charged pumice surface. Similar results were reported for removal of acidic red 88 from aqueous solution by agro-based waste material (pH 4.5) (Zarei, Pezhhanfar and Someh, 2017). Removal of nitrate from aqueous solution using scoria (pH =3) (Pirsaheb, Mohammadi and Moradi, 2016). Removal of Red reactive 2B by pumice (pH =3) (Asadi *et al.*, 2016). Up take of reactive black 5 by pumice and walnut activated carbon (pH =5) (Heibati, Rodriguez-Couto, *et al.*, 2014) and application of acidic treated pumice as an adsorbent for the removal of dye from aqueous solution (pH =3.5) (Zarrabi, 2012b).

Even though the pH is basic at pH =10, 57.1% and 60.2% removal efficiency was recorded using pumice and scoria respectively. This result may be due the presence of different functional groups such as OH, NH₂, CO and C-C. Similar result was reported for removal of tartrazine onto mixed waste activated carbon (adsorption capacity of 72.03 mg/g at pH 2 and 50.95 mg/g at pH of 10) (Habla *et al.*, 2014).

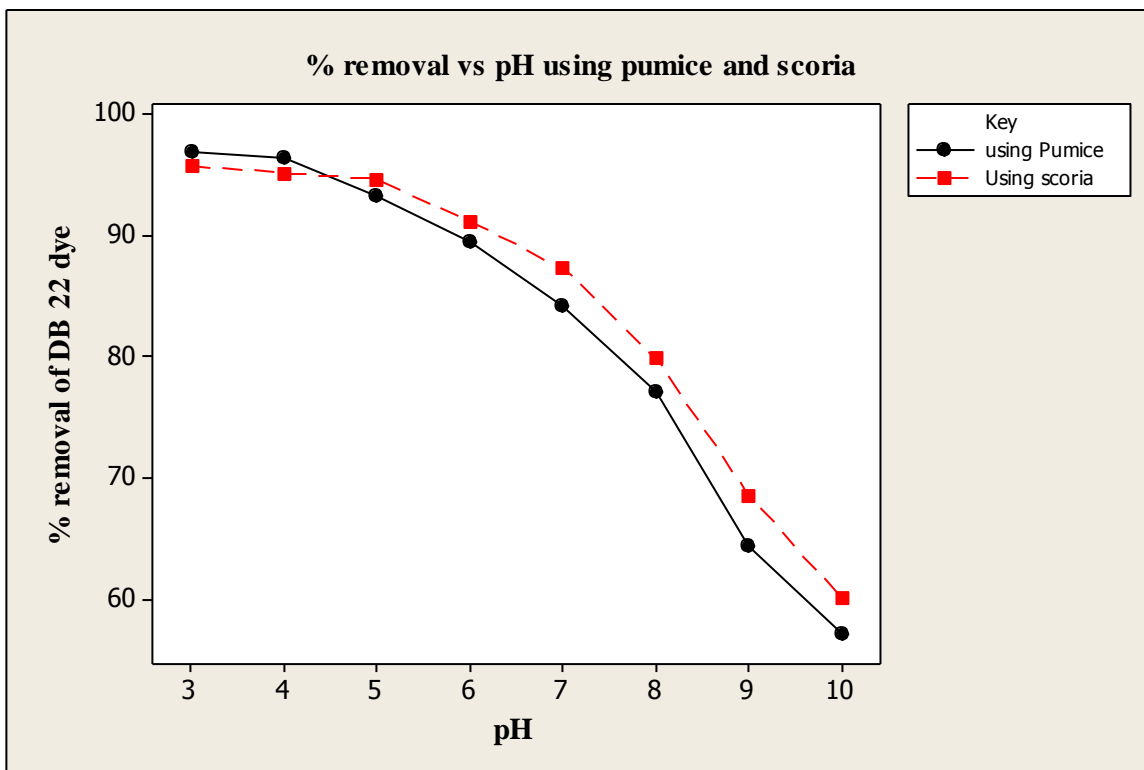


Figure 7: Effect of pH on the dye anion removal by pumice and scoria (initial dye concentration 50mg/L, time = 90min and 120 min, adsorbent dose =1.6 and 2g for pumice and scoria respectively)

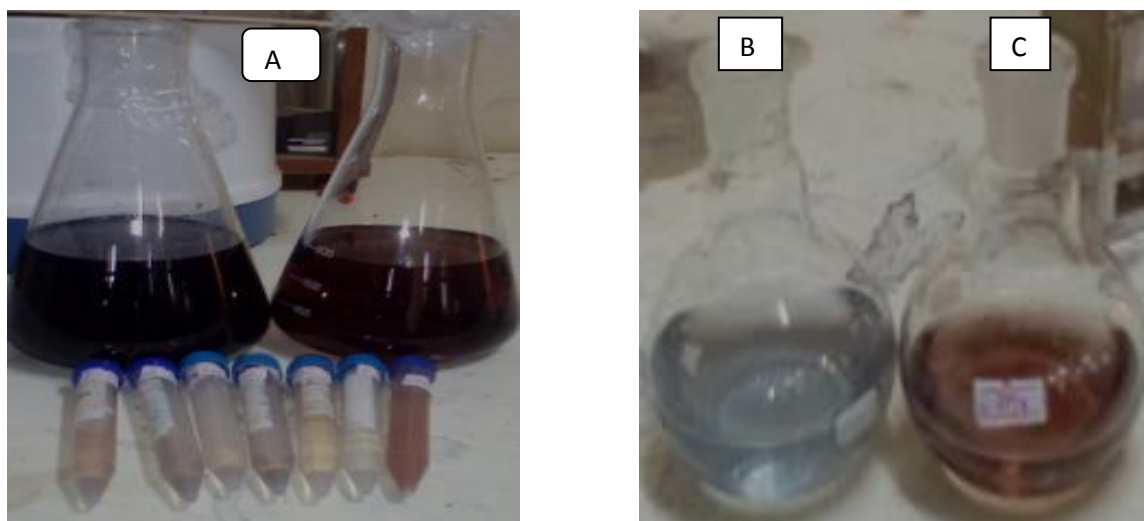


Figure 8: Decolonization before and after (A=before B= after agitated and centrifuged using pumice and C=after agitated and centrifuged using scoria but not filtered)



Figure 9 : Decolonization with different pH after agitated, centrifuged and filtered ready to read by spectrophotometry (A=control, B, C, D=pH (3, 7 and 10 using pumice and E, F and G=pH (3, 7 and 10 using scoria)

5.3. Effect of Initial Concentration of direct black 22 dye

The effect of initial dye concentration was investigated by varying the concentration of dye ion in the synthetic solution from 5 mg/L to 250 mg/L using 1.6g and 2g of adsorbent dose, 90 min and 120 min of time, pH 4 and 5 adjusted for pumice and scoria respectively.

The experimental result was indicated by Figure 10. As shown in Figure 10, direct black 22 dye ion adsorption efficiency decreases with an increase of initial concentration of direct black 22 dye. This effect is due to the increase of direct black 22 dye ion in the solution occupied more active sites of the adsorbent that decreases percent removal efficiency. Maximum removal efficiencies (95.1% and 93.8%) was observed up to concentration of 50 mg/L for which the concentration reduced to 2.45 mg/L and to 3.1mg/L using pumice and scoria. Moreover, the adsorption capacity was increased due to the availability of a higher number of dye ions per unit mass of the adsorbents.

There may be unoccupied binding sites on the adsorbent surface at a low dye concentration, and when the initial dye concentration increases, there will be insufficient sites for the

adsorption of dye molecules, thus decreasing the dye removal efficiency (Seow and Lim, 2016).

Similar study conducted on adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product showed that the diffusivity and activity of dye ions increased as its concentration increased (Banerjee and Chattopadhyaya, 2017). Similarly, this trend has been reported by; removal of methylene blue from aqueous solutions (Mupa, Rutsito and Musekiwa, 2016), removal of basic dyes from aqueous solution (Lafi et al., 2014), removal of acid red 88 from wastewater (Zarei, Pezhhanfar and Someh, 2017).

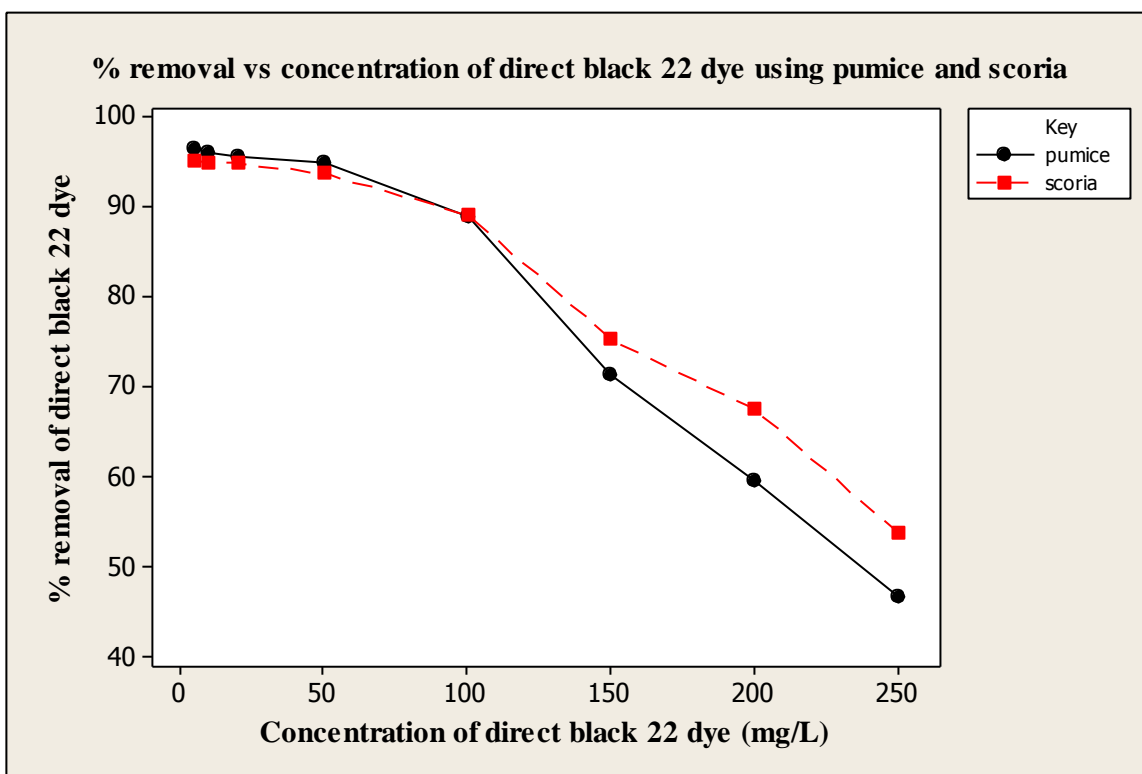


Figure 10:Effect of concentration on direct black 22 onto pumice and scoria(time=90min and 120min,adsorbent dose 1.6g and 2g using pumice and scoria respectively).

5.4. Effect of Adsorbent Dose

The effect of adsorbent dose on the dye removal efficiency was investigated with 0.4, 0.8, 1.2, 1.6, 2, 2.4 and 2.8 g. Batch adsorption studies were performed using initial dye concentration of 50 mg/L, particle size of adsorbents less than 1-3mm, agitation rate = 200 rpm, contact time 90 min and 120 min and pH 4 and 5 for pumice and scoria respectively at room temperature (22 ± 1) °C. It was observed that the dye adsorbed efficiency increases as a dose

of the adsorbent increased to 1.6g and 2.0g for pumice and scoria respectively and attained to maximum removal efficiency 96.1% and 94.4% for pumice and scoria respectively see Figure 11. Increasing adsorbent dosage will provide more surface area, there by leading to more binding sites for the adsorption of dye anion but adsorption capacity decreased sa dose increased because of the fixed initial dye concentration. This indicates that the number of active adsorption sites at higher dosage is large enough to accommodate dye ions (Seow and Lim, 2016). Similar results were reported for adsorptive removal of hazardous azorhodanine dye (Shoair and Mohamed, 2015), removal of reactive dye from aqueous solution using physico- chemically treated rice husk (Worku and Sahu, 2014).

However, when the dose increases beyond 1.6g and 2g for pumice and scoria respectively there is only slight improvement in the removal of dye ion in the solution. This suggests that this grams of adsorbents reduce 50mg/L of dye ion using pumice and scoria respectively in the aqueous solution used as the minimum dose for maximum adsorption (~96% and 94%) of 50 mg/L of direct black 22 dye ion in the aqueous solution to 1.9 mg/L and 2.8 mg/L using pumice and scoria respectively. Hence, 1.6g and 2.0g of pumice and scoria were selected as optimum dose for all further experiments respectively.

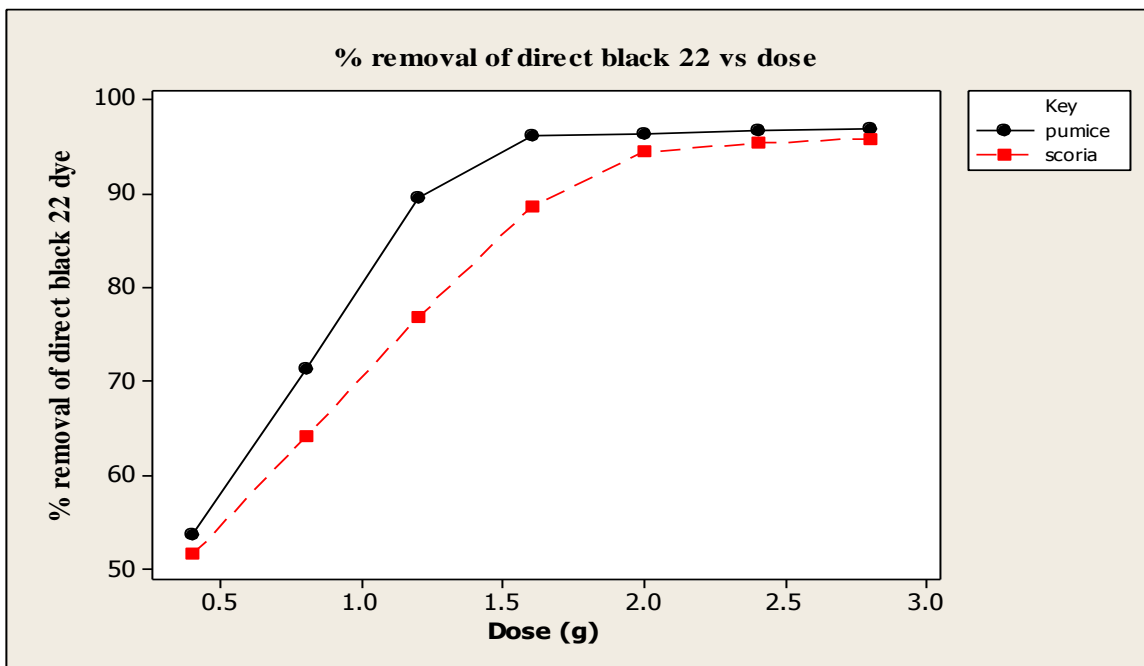


Figure 11: Effect of dose on the dye anion removal by pumice and scoria (time =90min and 120min, pH =4 and 5, initial dye concentration 50mg/L for pumice and scoria respectively

5.5. Effect of Agitation Time

The effects of agitation time on the adsorption of the direct black 22 dye onto pumice and scoria was carried out at 200 rpm to optimize the effective agitation time using both adsorbents. It was observed that an initial fast phase (0 – 30 min) where adsorption was rapid and contributed essentially to the equilibrium uptake of the direct black 22-dye. 94.6 % and 93.65 % pumice and scoria respectively and a second slow phase (30 – 90 min) whose contribution to equilibrium was relatively smaller with total amount of direct black 22 dyes adsorbed as 91.44 % and 91.32 % for pumice and scoria respectively as seen in Figure 12.

The first phase is an instantaneous phase, which is caused by external adsorption on to pumice and scoria. This was followed by slow phase, which was diffusion-controlled phase. The process of agitation of the adsorbate-adsorbent phase has the tendency of exposing active surfaces which otherwise, may be inaccessible. Therefore, 30 minute at 200rpm was taken as optimum agitation time for direct black 22 dye removal using pumice and scoria. Similar observation was earlier reported. Adsorption of alizarin and fluorescein dyes on adsorbent prepared from mango seed (first 30 minute) (Abdus-salam *et al.*, 2014) and Removal of nickel from aqueous solutions using Saudi activated bentonite (first 10 minute)(Al-Shahrani, 2012).

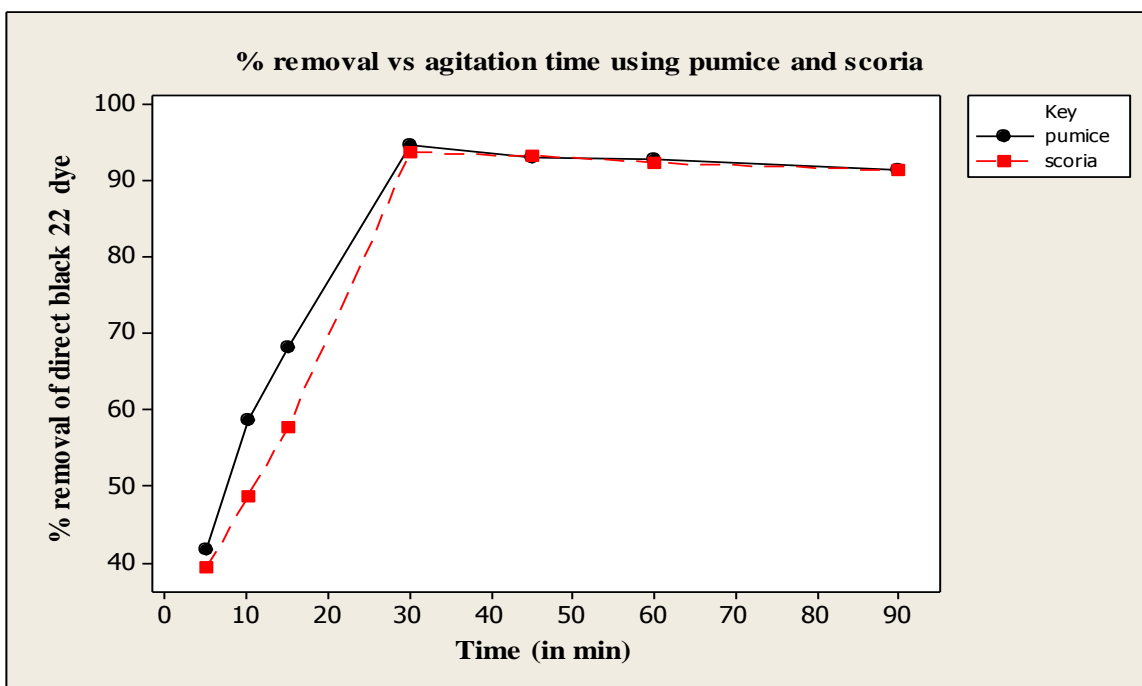


Figure 12: Effect of agitation time for direct black 22 50mg/L at 200 rpm using pumice and scoria

5.6. Adsorption Isotherm Study

The isotherm plots of the equilibrium adsorption of direct black 22 dye were graphically presented in Figure 13 and 14 Langmuir and Freundlich model for both adsorbents respectively for non-linearity. The values of the equilibrium constants computed from the isotherm models were given in Table 3 and 4 for Langmuir and Freundlich respectively with their related parameters. The isotherm model that describes direct black 22 dye onto pumice and scoria adsorption system was determined by evaluating the values of the coefficient of determination, R^2 , and Chi-squared test, χ^2 .

For the two models, q_e versus C_e plot was drawn from the experimental data of direct black 22 dye adsorption onto pumice and scoria. As seen in Table 3 and 4 and Figure 13 and 14 for Langmuir and Freundlich, high R^2 was derived by fitting the model with experimental data into the Langmuir isotherm model ($R^2 = 0.995$) and the Freundlich isotherm model ($R^2 = 0.89$) using pumice and Chi-squared of Langmuir was 0.046 which is less than Freundlich 1.06. A higher R^2 and smaller chi square indicates that the model better fit experimental data (Alebachew and Yadav, 2017). The Langmuir equation is valid for monolayer adsorption onto homogenous surface with a number of identical sites with interaction between adsorbed molecules using pumice and indicating that the model better satisfactorily described the sorption of direct black 22 dye onto pumice was chemisorption (Berger and Bhowan, 2011). The direct black 22 dye sorption capacity of pumice obtained at equilibrium from the Langmuir model was 7.71 mg/g, which was nearly the same with the maximum adsorption capacity obtained from the experimental data 7.3 mg/g). This was the maximum sorption capacity corresponding to complete monolayer coverage. Similar result was reported (Chen, 2015).

From the result, it was observed that the correlation coefficient value for the Freundlich model was slightly higher ($R^2 = 0.9899$) than Langmuir model ($R^2 = 0.971$) using scoria. Similarly, the Freundlich isotherm had smaller χ^2 value (0.109) than Langmuir model χ^2 value (0.314) using scoria. This indicates that the model satisfactorily described the sorption of direct black 22 dye on the scoria. Freundlich model was 8.1 mg/g, which was nearly the same with the maximum adsorption capacity obtained from the experimental data 8.8 mg/g). This indicates that the adsorption molecules onto non-energetically equivalent sites (heterogeneous) satisfactorily

described by physical adsorption (Anirudhan and Ramachandran, 2015). The computed value of the intensity of direct black 22 dye adsorption ($n= 3.34$ and $n =2.12$) using pumice and scoria respectively which was in the range of $0.1 < 1/n < 1$. This indicates that suitability and favorable adsorption of direct black 22 dye ions (Alebachew and Yadav, 2017). Moreover, the Langmuir isotherm model which is described in terms of the dimensionless constant called separation factor or equilibrium parameter (RL), obtained using the relation $RL= 1/ (1 + bco)$, is used to predict the nature of the adsorption process.

The values of RL calculated using equation 4 were from 0.16 to 0.9 using pumice and 0.2 to 0.92 using scoria verifying suitability favorability adsorption of direct black 22 dye on both adsorbents (Zarrabi, 2012a).

favorable	$0 < RL < 1$
unfavorable	$RL > 1$
linear	$RL = 1$
irreversible	$RL = 0$

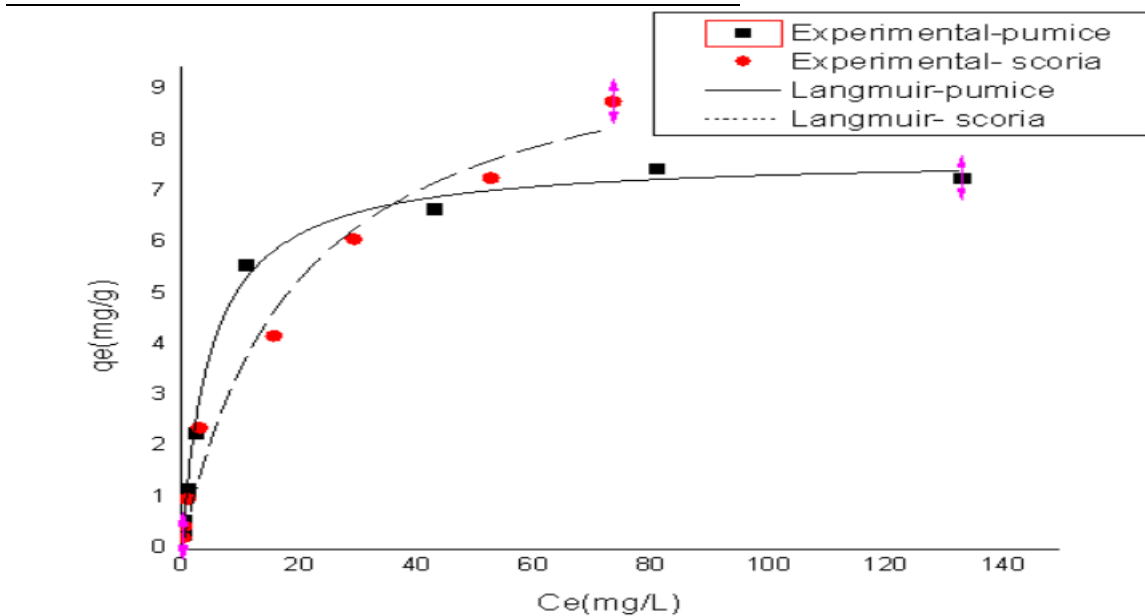


Figure 13: Langmuir non-linear isotherm model of adsorption of direct black 22 dye onto pumice and scoria

Table 3 : Langmuir non-linear isotherm equations and parameter

Parameters						
Langmuir				Statistics		
$q_e = (q_m * b * C_e) / (1 + b * C_e)$						
	Qm	B				
	Value	Error	Value	Error	χ^2	R ²
Pumice	7.717	0.155	0.20	0.020	0.046	0.995
Scoria	10.48	1.13	0.050	0.016	0.314	0.971

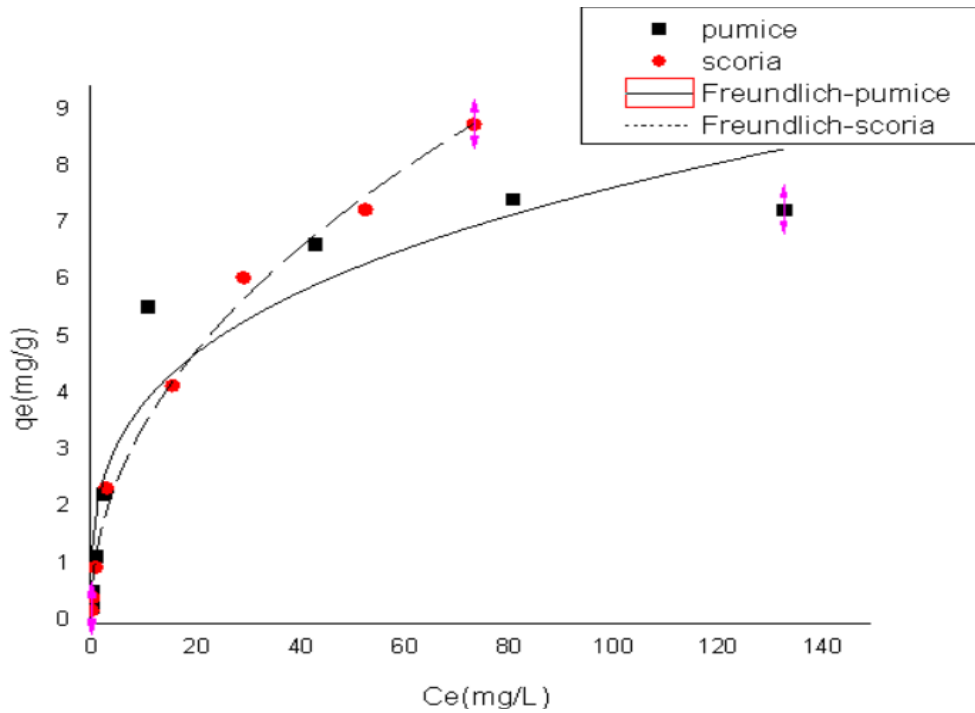


Figure 14: Freundlich non-linear isotherm model of adsorption of direct black 22dyes onto pumice and scoria

Table 4 : Freundlich non-linear isotherm equations and parameter

Kf	n	χ^2	R ²	
Pumice	1.936	3.34	1.06	0.8918
Scoria	1.163	2.12	0.109	0.9899

5.7. Adsorption Kinetics Study

Adsorption rate of solid surface depends on parameters like initial concentration of solute, active sites of the adsorbent and structural properties of the adsorbent (Zarrabi, 2012a).

The study of adsorption kinetics is very important to determine the rate constants for the reaction and to know how quickly or slowly the reaction is proceeding. To evaluate the kinetic parameters, Pseudo first order, Pseudo second order and intra particle were implemented to analyze the experimental data (Habiba *et al.*, 2014).

Initial direct black 22 dye concentration of 10 mg/L, 20mg/L and 40mg/L with adsorbent dose of 0.8g, 1.6g and 3.2g respectively was subjected to under similar conditions to study the adsorption kinetics.

5.7.1. Pseudo first order kinetics

The analysis of the kinetics data showed that the adsorption of DB 22 dye ion by pumice and scoria cannot be explained through the pseudo-first order kinetics (as seen Figure 15). Since the correlation coefficient value of pseudo first order kinetics obtained was low ($R^2 = 0.71$ and 0.81) when compared to pseudo-second order kinetic ($R^2 = 0.988$ and 0.993) see Figure 17 using pumice and scoria respectively. The summary parameters computed from the respective plot for the data was not presented for pseudo first order. In addition to this, since the plots of $\log(q_e - qt)$ versus t non-linear model the model cannot fit pseudo first order kinetics (Alebachew and Yadav, 2017).

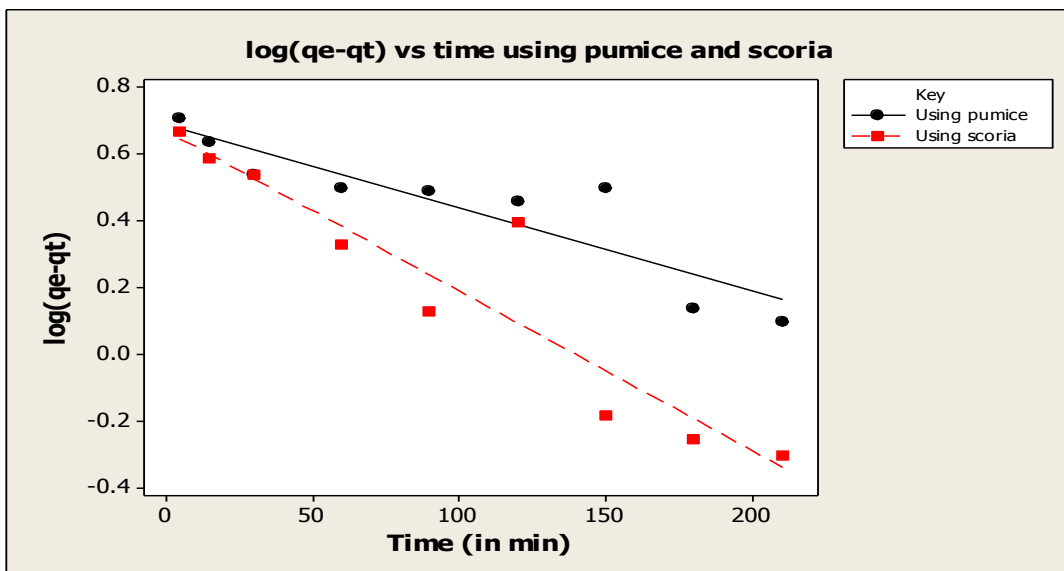


Figure 15: Plot of adsorption pseudo first order kinetics of direct black 22 dyes onto pumice and scoria ($R^2 = 0.71$ and 0.81 using pumice and scoria respectively)

5.7.2. Pseudo second order kinetics

Figure 16 shows pseudo second order kinetics plot at different initial direct black 22 dye concentration and Figure 17 shows the average pseudo second order kinetics plot of initial direct black 22 dye concentration.

From Table 5, it can be clearly seen that the rate constants for the three initial concentrations were very close. Therefore, the three constants were averaged to obtain a single rate constant, rate equation and correlation coefficient (Johnson, 2014).

The result seen from Figures 17 and Table 5 indicates that the reaction is described very well by pseudo-second order reaction mode with correlation coefficient of ($R^2 = 0.988$ and 0.993) using pumice and scoria respectively.

The highest R^2 values indicating that most satisfactory for describing the adsorption kinetics (Samarghandi *et al.*, 2013). Therefore, it can be concluded that based on the R^2 value, pseudo-second order kinetic model predicted as well suited for the whole adsorption process. Moreover, the plot of t/q_t versus t obtained was linear indicating applicability of this model (Balarak, Pirdadeh and Mahdavi, 2015b).

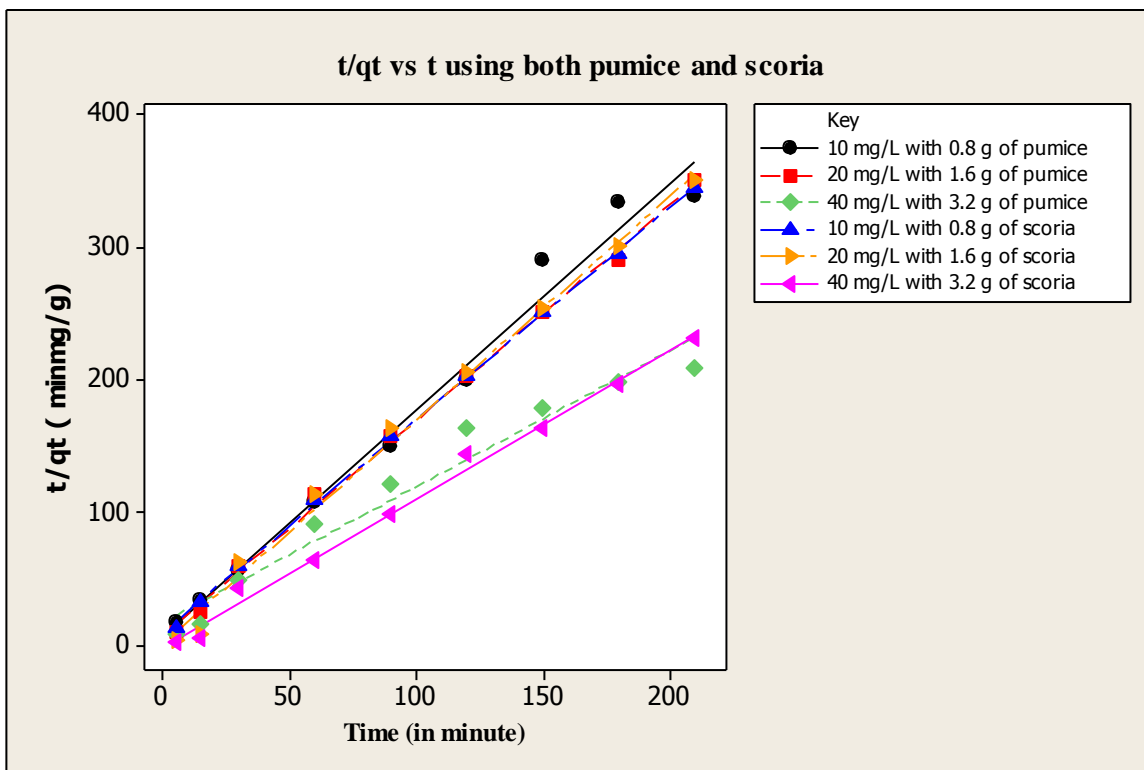


Figure 16: Linear pseudo second order kinetics for the adsorption of direct black 22 dye with initial concentrations 10,20,40 mg/L to adsorbent doses 0.8,1.6, and 3.2g respectively and (pH=4 and 5,time 90 min and 120 min using pumice and scoria respectively)

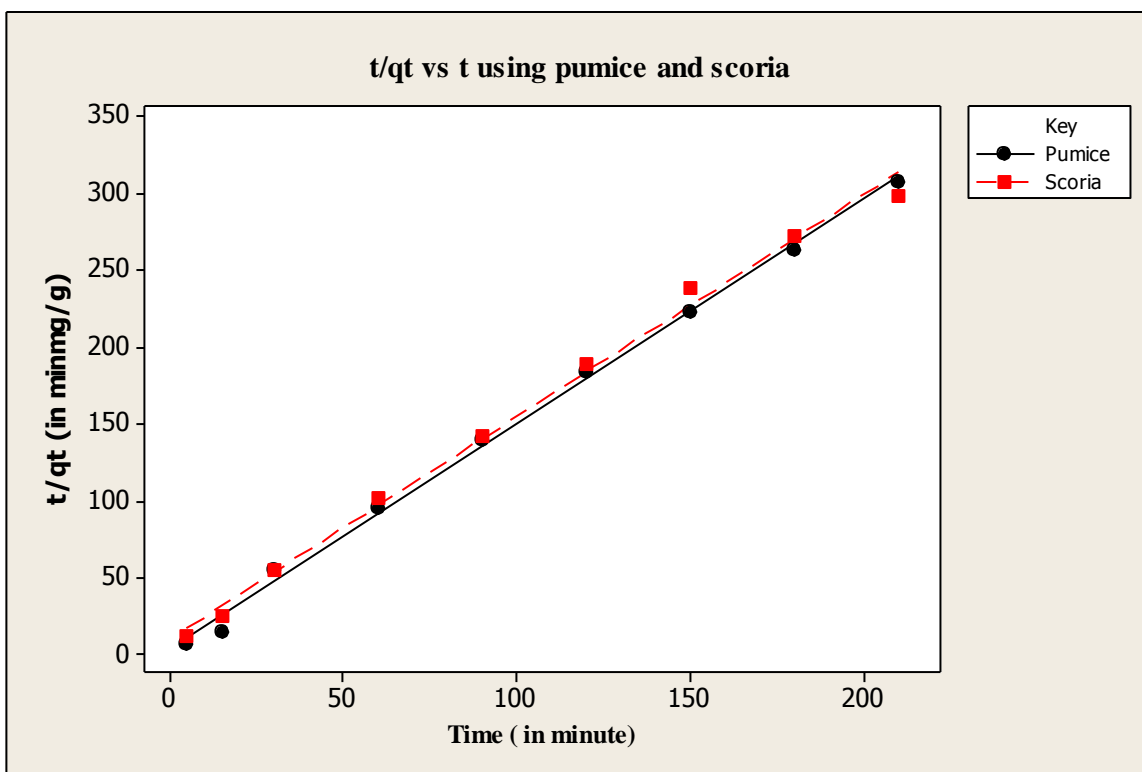


Figure 17: The average linear pseudo second order representation of direct black 22dyes onto pumice and scoria

Table 5: Linear pseudo second order equations and related parameters

Co mg/L	Adsorb ent g/mgmin	K ₂ g/mgmin	Pumice		Scoria		
			t/qt=1/k ₂ qe ² +t/qe Rate equation	R ²	t/qt=1/k ₂ qe ² +t/qe Rate equation	R ²	
10	0.8	4X 10 ⁻³	t/qt = 5.1 + 1.71t	0.973	2 X 10 ⁻³	t/qt = 14.4 + 1.57 t	0.989
20	1.6	1X10 ⁻³	t/qt = 15.1 + 1.57t	0.998	1.1X10 ³	t/qt = 17.3 + 1.5 t	0.991
50	2	4X10 ⁻³	t/qt = 10.4 +0.74 t	0.994	1X10 ⁻³	t/qt=8.96+0.800t	0.999
Average		3X10 ⁻³	t/qt=10.2+1.34t	0.988	1.3X10 ⁻³	t/qt=13.5+ 1.31t	0.993

5.7.3 Intra-particle diffusion

The correlation coefficient value of intra particle diffusion obtained was low ($R^2 = 0.83$ and 0.86) when compared to pseudo-second order kinetic ($R^2 = 0.988$ and 0.993) using pumice and scoria respectively.

To be the rate-limiting step of direct black 22 dye removal is the intra-particle diffusion, the plot of qt against the $t^{1/2}$ should be a straight line and pass through the origin (Alebachew and Yadav, 2017). Therefore, we concluded that the linear portion of the curve did not pass through the origin. This indicates that the direct black 22 dye adsorption onto pumice and scoria is a complex process and the intra-particle diffusion was not the only rate controlling step. Figure 18 and 19 shows the plot of qt against the $t^{1/2}$ for both pumice and scoria on the removal of direct black 22 dyes respectively.

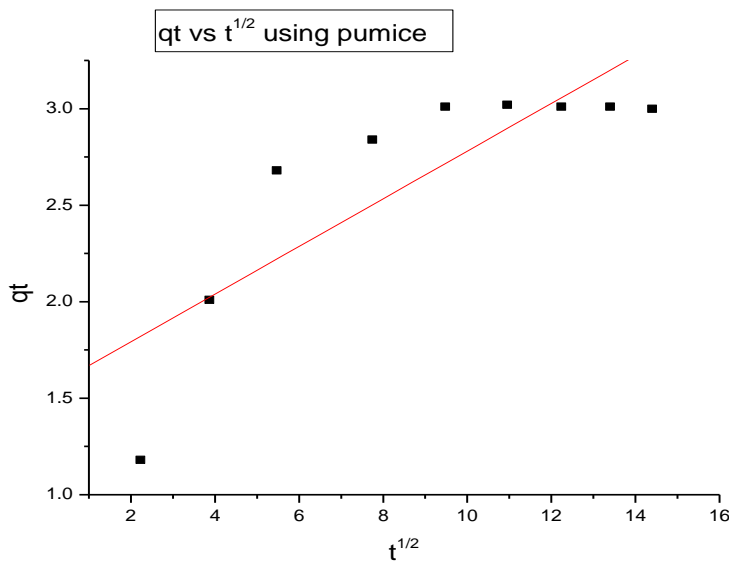


Figure 18: Plot of qt vs $t^{1/2}$ ($R^2 = 0.83$ using pumice)

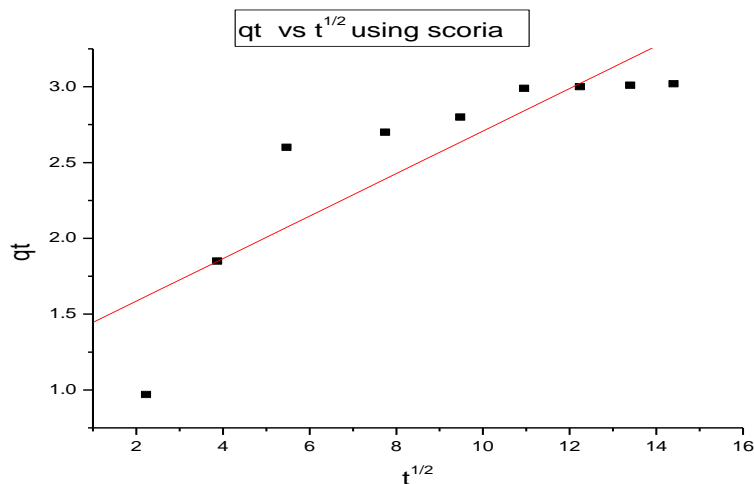


Figure 19: Plot of qt vs $t^{1/2}$ ($R^2=0.86$ using scoria)

5.8. Effect of interfering ions

The data reported in the previous sections was only containing the aqueous solutions of direct black 22 ions. However, dye contaminated surface water typically contains also several other anions that can affect the adsorption process and compete with the dye ions for adsorption.

In order to understand the effect of interfering anions, additional adsorption experiments were carried out in presence of 50 mg/Salt solutions of chloride (Cl^-), Fluoride(F^-) nitrate (NO_3^-), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}), separately and in a mixture using pumice and scoria. Cl^- , F^- , SO_4^{2-} , NO_3^- , HCO_3^- and PO_4^{3-} ions, separately as well as the mixture of these anions with direct black 22 dye having concentration of 50mg/L using 1.6 g and 2g of pumice and scoria respectively as seen in Figure 20..

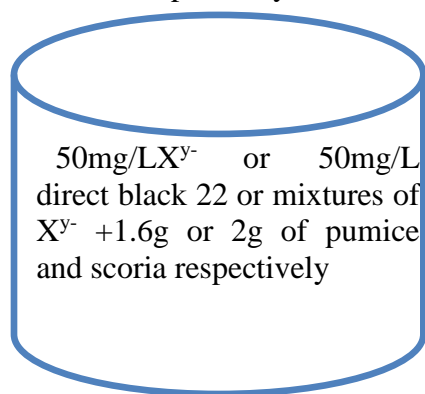


Figure 20: Experimental procedure to determine the major interfering anions of direct black 22 dye

Where $X^{y-} = Cl^- / F^- / NO_3^- / HCO_3^- / SO_4^{2-} / PO_4^{3-}$ added separately and all anions together.

The experimental procedures were carried out to identify the most competing anion of black direct black 22 dye. Minimum removal efficiency of the dye was obtained when F^- , Cl^- , SO_4^{2-} and PO_4^{3-} were added with removal efficiency of direct black 22 dye 53.2, 55.6, 64.1 and 61.5% using pumice respectively. For scoria, the values were 47.8, 49.7, 64.2 and 55.6% with Cl^- , SO_4^{2-} , NO_3^- and PO_4^{3-} respectively. With all mixture of anions, 33.2% and 29.6% and without interfering anions 96.01 and 95.5% using pumice and scoria respectively as seen in figure 21. This result indicates that a negative effect on the removal of direct black 22 dye in the presence of these anions. The removal decreased as charge of interfering anion increased and affinity of anions (Asere, Mincke, De Clercq, *et al.*, 2017). As seen in figure 21 the effect is high when PO_4^{3-} , SO_4^{2-} , Cl^- and F^- was used.

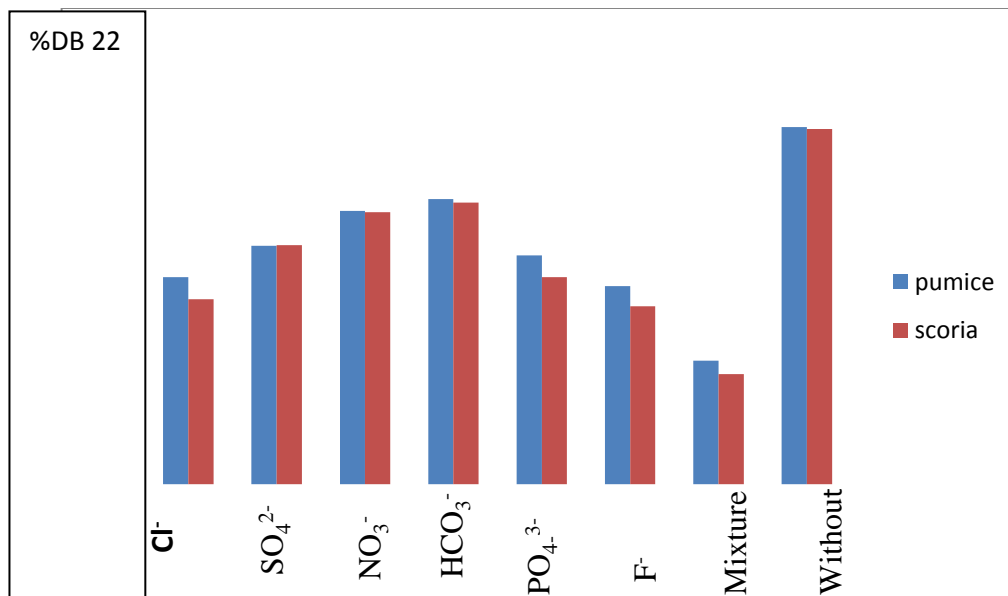


Figure 21: Effects of co-existing anions on adsorption of direct black 22 dyes using pumice and scoria

5.9. Applicability of pumice and scoria as adsorbents in Textile real sample

The adsorption experiment for direct black 22 dye ion from waste water on to pumice and scoria was carried out in triplicate without adjusting the pH of the water sample (pH=6.2) using (1.6 to 2.8) g dose of pumice and scoria respectively with particle size of less than 1-3 mm. The result showed that the direct black 22 dye removal efficiency from waste water with initial dye concentration of 62.2mg/L (which was taken from Ayka Addis) was reduced to

19.2mg/L 23.8mg/L (68.8 and 61.3%) when using the optimum dose(1.6 and 2g) used for the synthetic water using pumice and scoria respectively.

However, 2.8g of pumice and scoria reduced 62.2g/L to 7.01 and 12.5 mg/L of direct black 22 dye ion (88.4%and 79.4%) as seen in figure 20.From this, it can be concluded that such wastewater requires high dose of pumice/scoria to scale down the more concentrated direct black 22 dye ion to permissible limit. This is due to the presence of a wide variety of other ions in wastewater, and may compete with direct black 22 dye ion for adsorption on pumice and scoria. Some of the ion present in sample of wastewater used for the investigation was listed in table 6 with respect to their concentration. This is due to the higher competing effect of these co-existing anions for the active sites of the adsorbents. Sulfate and chloride are the dominant anions in the sample. The impact of chloride is more due to the formation of outer sphere complexes and has high affinity whereas the sulfate showed the less impact than the chloride. Therefore, chloride was the anion that caused the greatest reduction in direct black 22 dye adsorption, as was also reported in other studies for various adsorbents (Reddy and Mohammed, 2016) and (Johnson, 2014).

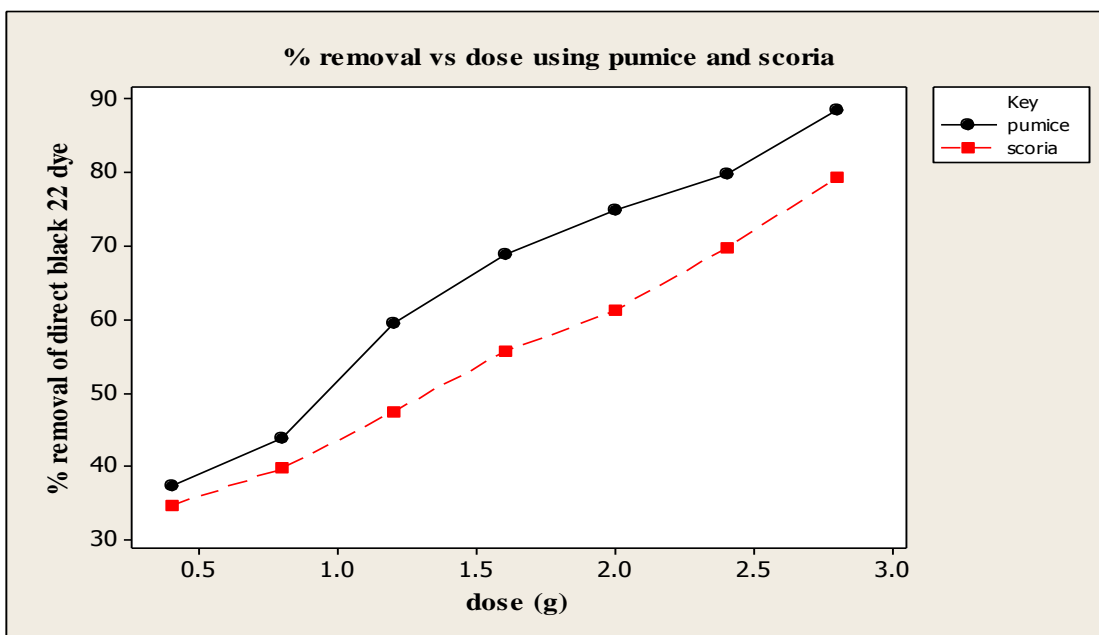


Figure 22: Dose vs percentage removal efficiency of direct black 22 dye in real sample at (pH =6.4, concentration of dye 62.2mg/L, time =90min and 120 min using pumice and scoria respectively)

Table 6: Physicochemical characteristics Textile wastewater used for experiment

Physicochemical parameters	Values	Maximum limit	References
Turbidity (NTU)	16.31	NA	EEPA,2004
Conductivity ($\mu\text{S/cm}$)	430	NS	EEPA ,2004
Water temperature ($^{\circ}\text{C}$)	26	<25	WHO ,2009
DO(mg/L)	6.7	>10	WHO, 2009
COD(mg/L)	2166	150	EEPA, 2004
BOD(mg/L)	1700	50	EEPA, 2004
Chloride (mg/l, Cl^-)	973	>250detectable taste	WHO,2003
Sulfate (mg/L)	591	200	EPA, 2003
Fluoride (mg/L)	0.34	1.5	WHO,2011
Orthophosphate (mg/L)	None	10	EPA, 2003
Nitrate (mg/L)	15.1	50	EPA, 2003
Carbonate (mg/L, CO_3^{2-})	None	>180	EPA,1994a
Bicarbonate(mg/L, HCO_3^-)	0.94	>180	EPA,1994a
pH	6.2	6-9	EEPA, 2003
Direct black 22 dye(mg/L)	62.2	30	EPA, 2006
Ambient temperature ($^{\circ}\text{C}$)	22		Source:(Hessel et al., 2018)

5.10. Desorption of direct black 22 dye from pumice and scoria Surfaces

Desorption is the key to manage the residue of dye from the environment because the DB 22 dye which was unconfined to aqueous environment can pollute the environment. Desorption was tested using 0.1N of NaOH at pH 11(Samarghandi et al., 2013).

The percentage of direct black 22 dyes that could be desorbed were 42.6-59.4% and 49.4-68.9% for pumice and scoria respectively. Desorption was studied in 3 adsorption desorption cycles. Even in the third cycle $\approx 42\%$ using pumice and $\approx 49\%$ using scoria of the direct black 22 dyes was retained. Almost similar result was reported for the removal of Acid Red 14 (AR 14) and Acid Red 18 (AR 18) (Reza Samarghandi et al., 2012). In basic solutions, the electrostatic interaction between adsorbents (pumice and scoria) and the dye anion (direct black 22) becomes much weaker due to the neutralization of positively charged groups. As a result, the adsorbed dye ion leaves the adsorption site of pumice and scoria.

Table 7: Comparison of different adsorbents and different dyes with direct black 22

Adsorbent	Time	Dose	P ^H	Co	Adsorbate	qm	Reference
modified bentonite clay	240 min	0.1 g	9	40mg/L	Methylene blue	3.99 mg/g	(Anirudhan and Ramachandran, 2015)
Lemna minor biomass	75 min	6 g	3	25mg/L	Acid red 88	7.8mg/g	(Balarak, Pirdadeh and Mahdavi, 2015a)
Orange peel	15 hr	0.3g		30mg/L	Brilliant blue	2.2 mg/g	(M.Mafra <i>et al.</i> , 2013)
Activated Algerian clay	30 min	0.8g	9	26.2 mg/L	Methyl orange	32.57 mg/g	(Djelloul Bendaho et al., 2017)
Pumice	90 min	1.6 g	4	50mg/L	Direct black 22	7.71 mg/g	This study
Scoria	120 min	2 g	5	50mg/L	Direct black 22	8.1 mg/g	This study

CHAPTER SIX

6. CONCLUSION AND RECOMMENDATION

6.1. Conclusion

The naturally available pumice and scoria can remove direct black 22 dyes from aqueous solution. Compare to pumice from the experimental result, Scoria prefer less acidic to release the treated water to the environment because the optimum pH of pumice was 4 which is more acidic than pH 5 which was the optimum pH of scoria. Optimum parameters of pH 4 and 5, adsorbent dose of 1.6g and 2g, equilibrium time 90 min and 120 minutes, agitation time 30 minutes at 200 rpm and room temperature (22 ± 1) were used to investigate the adsorption capacity of pumice and scoria respectively. Results of the study indicates that 50 mg/L direct black 22 anion concentrations reduced to 2.45mg/L and 3.1 mg/L from aqueous solutions using pumice and scoria respectively. It can be concluded that wastewater analyzed for adsorption required high dose of pumice/scoria to scale down the more concentrated direct black 22 dye compared to synthetic direct black 22 dyes. This is due to the presence of a wide variety of other ions in wastewater, and competes with direct black 22-dye ion for adsorption onto pumice and scoria. The Langmuir model equilibrium data best fit to adsorption isotherm with a maximum adsorption capacity of 7.71mg/g using pumice with correlation coefficient R^2 0.995 and smaller χ^2 0.046 with maximum adsorption capacity 8.1 mg/g. Direct black 22 ion uptake well fitted with pseudo-second order model with correlation coefficient R^2 (0.988 and 0.993) using pumice and scoria respectively. Freundlich model better fit the experimental data with correlation coefficient 0.9899 and smaller χ^2 value (0.109) using scoria.

6.2. Recommendation

Based on the experimental result that was conducted for the removal of direct black 22 dye ion from aqueous solution and wastewater by pumice and scoria as adsorbents the following recommendations are pointed out: -

Since the adsorbents were effective at pH 4 and 5 using pumice and scoria respectively, it is better if removal efficiency is around neutral pH to discharge the treated water to the environment. Treating the adsorbents with weak acid is better.

Moreover, the maximum concentration 50mg/L was reduced to 2.45mg/L and 3.1mg/L using pumice and scoria respectively, which is still not completely removed therefore, some modification of adsorbents is recommended to get more surface area.

During applicability of this adsorbent to real water situation, it consumes large amount of adsorbent due to the presence of wide variety of ions that competes the active adsorbent site. Thus, it is advisable to remove the major interfering ions and mixture of cofactors with suitable pretreatment techniques and it is also better to optimize the critical parameters such as pH, the dose of adsorbent and time during treatment.

7. References

- Abdurrahman, F. Bin, Akter, M. and Abedin, M. Z. (2013) 'Dyes Removal From Textile Wastewater Using Orange Peels', 2(9).
- Abdus-Salam, Nasiru B and Magaji. (2014) 'Adsorption of Alizarin and Fluorescein Dyes on Adsorbent prepared from Mango Seed', 15(1), pp. 232–244.
- Al-Shahrani, S. S. (2012) 'Removal of nickel from aqueous solutions using Saudi activated bentonite', *WIT Transactions on Ecology and the Environment*, 167, pp. 461–471. doi: 10.2495/ST110411.
- Alebachew, N. and Yadav, O. P. (2017) 'Removal of Phenol Red Dye From Contaminated Water Using Barley (*Hordeum vulgare* L .) Husk-Derived Activated Carbon'. doi: 10.17311/sciintl.2017.7.16.
- Alexandrica, Maria C and Mihaela Hritcu. (2015) 'Layered Double Hydroxides As Adsorbents For Anionic Dye Removal From Aqueous Solutions', 14(2), pp. 381–388.
- Ali, M. A. (2013) 'Australian Journal of Basic and Applied Sciences Chemical , Physical and Geotechnical Properties Comparison between Scoria and Pumice Deposits in Dhamar – Rada Volcanic Field -SW Yemen', 7(11), pp. 116–124.
- Anirudhan, T. S. and Ramachandran, M. (2015) 'Adsorptive removal of basic dyes from aqueous solutions by surfactant modified bentonite clay (organoclay): Kinetic and competitive adsorption isotherm', *Process Safety and Environmental Protection*. Institution of Chemical Engineers, 95, pp. 215–225. doi: 10.1016/j.psep.2015.03.003.
- Asadi, Abdollah A and Ali M. (2016) 'Red Reactive 2 Dye Removal from Aqueous Solutions by Pumice as a Low-Cost and Available Adsorbent', 5(3), pp. 145–152.
- Asere, T. G., Mincke, S., De Clercq, J., et al. (2017) 'Removal of arsenic (V) from aqueous solutions using chitosan–red scoria and chitosan–pumice blends', *International Journal of Environmental Research and Public Health*, 14(8), pp. 1–19. doi: 10.3390/ijerph14080895.
- Ashtaputrey, P. D. and Ashtaputrey., S. D. (2016) 'Removal of Dye From Aqueous Solution By Pineapple Peel Activated Carbon As an Adsorbent.', *International Journal of Advanced Research*, 4(10), pp. 1513–1518. doi: 10.21474/IJAR01/1957.
- Djelloul Bendaho, Tabet Ainad Driss and Djillali Bassou (2017) 'Adsorption Of Acid Dye Onto Activated Algerian Clay', 31(1), pp. 51–62.

- Balarak, D., Pirdadeh, F. and Mahdavi, Y. (2015b) 'Biosorption of Acid Red 88 dyes using dried Lemna minor biomass', 1(2), pp. 81–90.
- Banerjee, S. and Chattopadhyaya, M. C. (2013) 'Adsorption characteristics for the removal of a toxic dye , tartrazine from aqueous solutions by a low cost agricultural by-product Adsorption characteristics for the removal of a toxic dye , tartrazine from aqueous solutions by a low cost agricultural by', (May 2015). doi: 10.1016/j.arabjc.2013.06.005.
- Banerjee, S. and Chattopadhyaya, M. C. (2017) 'Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product', Arabian Journal of Chemistry, 10(May 2015), pp. S1629–S1638. doi: 10.1016/j.arabjc.2013.06.005.
- Benkhaya, S., Harfi, S. El and Harfi, A. El (2018) 'Classifications , properties and applications of textile dyes : A review', (March).
- Berger, A. H. and Bhowan, A. S. (2011) 'Comparing Physisorption and Chemisorption Solid Sorbents for use Separating CO 2 from Flue Gas using Temperature Swing Adsorption', *Energy Procedia*. Elsevier, 4, pp. 562–567. doi: 10.1016/j.egypro.2011.01.089.
- Bhatt, P. and Rani, A. (2013) 'Textile dyeing and printing industry: An environmental hazard', *Asian Dyer*, 10(6), pp. 51–54. doi: 10.4236/ns.2012.41004.
- Birhanie, M., Leta, S. and Khan, M. M. (2017) 'Treatment of Tannery Wastewater to Remove Hazardous Pollutants by Scoria (Volcanic ash) a Low cost Adsorbent', (6), pp. 2841–2849.
- Brandi, J. and Wilson-Wilde, L. (2012) 'Standard Methods', in *Encyclopedia of Forensic Sciences: Second Edition*, pp. 522–527. doi: 10.1016/B978-0-12-382165-2.00237-3.
- Carmen, Z. and Daniela, S. (2010) 'Textile Organic Dyes – Characteristics , Polluting Effects and Separation / Elimination Procedures from Industrial Effluents – A Critical Overview'.
- Chen, X. (2015) 'Modeling of Experimental Adsorption Isotherm Data', pp. 14–22. doi: 10.3390/info6010014.
- Chequer, F. M. D., Dorta, D. J. and Oliveira, D. P. De (2011) 'Azo Dyes and Their Metabolites : Does the Discharge of the Azo Dye into Water Bodies Represent Human and Ecological Risks ?', *Advances in Treating Textile effluent*, pp. 27–48. doi: 10.5772/19872.
- Desta, M. B. (2013) 'Batch Sorption Experiments : Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (Eragrostis tef)

- Agricultural Waste', 2013.
- Ferreira, E. S. B., Hulme, A. N. and Quye, A. (2004) 'The Natural Constituents of Historical Textile Dyes The natural constituents of historical textile dyes', (August). doi: 10.1039/b305697j.
- 'General introduction to the chemistry of dyes' (2010) in *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, pp. 55–67. doi: 10.1016/j.chemosphere.2003.10.046.
- Habila, M. A. *et al.* (2014) 'Removal of Tartrazine Dye onto Mixed-Waste Activated Carbon: Kinetic and Thermodynamic Studies', *Clean - Soil, Air, Water*, 42(12), pp. 1824–1831. doi: 10.1002/clen.201300191.
- Habte, H., Zewge, F. and Redi, M. (2014) 'Removal of azo dye from water by adsorption using waste residue from alum manufacturing process', *African Journal of Environmental Science and Technology*, 8(9), pp. 482–490. doi: 10.5897/AJEST2014.1674.
- Hassaan, M. A. and Nemr, A. El (2017) 'Health and Environmental Impacts of Dyes : Mini Review', 1(3), pp. 64–67. doi: 10.11648/j.ajese.20170103.11.
- Heibati, B., Rodriguez-couto, S., *et al.* (2014) 'Journal of Industrial and Engineering Chemistry Uptake of Reactive Black 5 by pumice and walnut activated carbon : Chemistry and adsorption mechanisms', *Journal of Industrial and Engineering Chemistry*. The Korean Society of Industrial and Engineering Chemistry, 20(5), pp. 2939–2947. doi: 10.1016/j.jiec.2013.10.063.
- Heibati, B., Rodriguez-Couto, S., *et al.* (2014) 'Uptake of Reactive Black 5 by pumice and walnut activated carbon: Chemistry and adsorption mechanisms', *Journal of Industrial and Engineering Chemistry*. The Korean Society of Industrial and Engineering Chemistry, 20(5), pp. 2939–2947. doi: 10.1016/j.jiec.2013.10.063.
- Hessel, C,Allegre, C,Maisseu, M Charbit and F Moulin. (2018) 'Guidelines and legislation for dye house effluents Guidelines and legislation for dye house effluents', (May 2007). doi: 10.1016/j.jenvman.2006.02.012.
- Joshi, M., Bansal, R. and Purwar, R. (2004) 'Colour removal from textile effluents', *Indian Journal of Fibre and Textile Research*, 29(2), pp. 239–259. doi: 10.1016/0043-1354(91)90006-C.

- Journal, Brazilian, Mafra, M R, Zuim, D R, Ferreira and M A. (2013) 'Adsorption Of Remazol Brilliant Blue On An Orange Peel Adsorbent', 30(3), Pp. 657–665.
- Kechi, A., Chavan, R. B. and Moeckel, R. (2013) 'Ethiopian Dye plants As a Source of Natural Dyes for Cotton Dyeing Abstract ', 3(4), pp. 501–510.
- Khaniabadi, Y. O. *et al.* (2017) 'Removal of Congo red dye from aqueous solutions by a low-cost adsorbent: activated carbon prepared from Aloe vera leaves shell', *Kerman University of Medical Sciences*, 4(1), pp. 29–35. doi: 10.15171/EHEM.2017.05.
- Kravić, Jaroslava, Zorica and Pucarević. (2010) 'Determination of trans fatty acids in foodstuffs by gas chromatography-mass spectrometry after simultaneous microwave-assisted extraction-esterification', *Journal of the Serbian Chemical Society*, 75(6), pp. 803–812. doi: 10.2298/JSC090717051K.
- Lafi, Amor Hameed and B. H. (2014) 'Removal of basic dyes from effluent waste as potential adsorbent for the aqueous solution', *Korean Journal of Chemical Engineering*, 31(12), pp. 2198–2206. doi: 10.1007/s11814-014-0171-7.
- Lavanya, C. (2014) 'Review Article Degradation of Toxic Dyes: A Review', *International Journal of Current Microbiology and Applied Sciences*, 3(6), pp. 189–199.
- Mehari, A. K., Gebremedhin, S. and Ayele, B. (2015) 'Effects of Bahir Dar Textile Factory Effluents on the Water Quality of the Head Waters of Blue Nile River, Ethiopia', 2015.
- Mohammad, S. and Azeez, A. (2005) 'HPLC Determination of Four Textile Dyes and Studying Their Degradation Using Spectrophotometric Technique', *An-Najah National University Faculty Of Graduate Studies*, pp. 1–110. doi: 10.1017/CBO9781107415324.004.
- Mohammad Razi, M. A., Mohd Hishammudin, M. N. A. and Hamdan, R. (2017) 'Factor Affecting Textile Dye Removal Using Adsorbent From Activated Carbon: A Review', *MATEC Web of Conferences*, 103, p. 6015. doi: 10.1051/mateconf/201710306015.
- Mohammed, M. a, Shitu, A. and Ibrahim, A. (2014) 'Removal of Methylene Blue Using Low Cost Adsorbent: A Review', *Research Journal of Chemical Sciences*, 4(1), pp. 91–102.
- Moradi, Lida P and Kiomars. (2015) 'Removal of Hexavalent Chromium from Aqueous Solution by Powdered Scoria-Equilibrium Isotherms and Kinetic Studies PhD Student of Environmental Health Engineering Faculty, PhD Student of Environmental Health Engineering Faculty ', 33(3), pp. 393–400. doi: 10.5829/idosi.wasj.2015.33.03.74.

- Moutinho, I. L. D., Bertges, L. C. and Assis, R. V. C. (2007) 'Prolonged use of the food dye tartrazine (FD&C yellow no 5) and its effects on the gastric mucosa of Wistar rats.', *Brazilian journal of biology = Revista brasleira de biologia*, 67(1), pp. 141–5. doi: 10.1590/S1519-69842007000100019.
- Mupa, M., Rutsito, D. D. and Musekiwa, C. (2016) 'Removal of methylene blue from aqueous solutions using biochar prepared from Eichhornia crassipes (Water Hyacinth)-molasses composite: Kinetic and equilibrium studies', *African Journal of Pure and Applied Chemistry*, 10(6), pp. 63–72. doi: 10.5897/AJPAC2016.0703.
- NPTEL - National Programme on Technology Enhanced Learning (2014) 'Toxicity of dyestuffs', pp. 1–21.
- Of, R. *et al.* (2016) 'Removal Of Methylene Blue Dye From Aqueous Solutions By Mosambi Fruit Peel Geethapriya D and Barathan S Department of Physics , Faculty of Science , Annamalai University , Annamalai University-608002', 7, pp. 13452–13457.
- Ouezzani, I., Hourch, A. El and Azzouzi, M. El (2016) 'CODEN (USA): PCHHAX Photodegradation of toxic synthetic food coloring : The Tartrazine .', 8(1), pp. 39–43.
- Panić, V. V *et al.* (2013) 'Adsorption of azo dyes on polymer materials', pp. 881–900. doi: 10.2298/HEMIND121203020P.
- Parashar, C. (2012) 'Removal of Malachite Green dye by adsorption using char', (108).
- Petzoldt, T. L. (2014) 'The Effect of Azo Textile Dyes on Gross Primary Production and Community Respiration in an Artificial Environment The Effect of Azo Textile Dyes on Gross Primary'.
- Pirsaheb, M., Mohammadi, H. and Moradi, M. (2016) 'Survey of effective parameters on efficiency of scoria as a low cost adsorbent for removal of nitrate from aqueous solution', *International Journal of Pharmacy and Technology*, 8(4), pp. 22773–22780.
- Razi, M. A. M., Hishammudin, M. N. A. and Hamdan, R. (2017) 'Factor affecting textile dye removal using adsorbent from activated carbon : A review', *MATEC Web of Conferences 103*, 6015, pp. 1–17. doi: 10.1051/mateconf/201710306015.
- Reddy, D. and Mohammed, N. (2016) 'A Low Cost Modified Porous Lava (Pumice Stone) for Water Purification', (September). doi: 10.1166/mat.2015.1258.
- Reza Samarghandi, M. *et al.* (2012) 'Application of acidic treated pumice as an adsorbent for the removal of azo dye from aqueous solutions: Kinetic, equilibrium and thermodynamic

- studies', *Iranian Journal of Environmental Health Science and Engineering*, 9(9). doi: 10.1186/1735-2746-9-9.
- Samarghandi, M. R. *et al.* (2013) 'Removal of Acid Black Dye By Pumice Stone As a Low Cost Adsorbent: Kinetic, Thermodynamic and Equilibrium Studies', *Environmental Engineering and Management Journal*, 12(11), pp. 2137–2147. Available at: <http://omicron.ch.tuiasi.ro/EEMJ/>.
- Seow, T. W. and Lim, C. K. (2016) 'Removal of dye by adsorption: A review', *International Journal of Applied Engineering Research*, 11(4), pp. 2675–2679.
- Shoair, A. F. and Mohamed, A. S. (2015) 'Adsorptive removal of hazardous azorhodanine dye from an aqueous solution using rice straw fly ash', 6(6), pp. 1723–1732.
- Soresa, M. (2011) 'Ayka Addis Textile Wastewater Treatment by the Fenton's Reagent', pp. 1–73.
- Johnson, A. (2014) 'Synthesis, characterization and development of aluminium hydroxide – based adsorbents for defluoridation of drinking water'.
- Tegegn, F. E. (2012) *Physico-chemical pollution pattern in Akaki River basin , Addis Ababa , Ethiopia*. Available at: <http://www.diva-portal.org/smash/get/diva2:555414/fulltext02>.
- Worku, A. and Sahu, O. (2014) 'Removal of Reactive Dye from Aqueous Solution Using Physico- Chemically Treated Rice Husk', 2(3), pp. 77–84.
- Yapar, S. (2015) 'Dye Removal From Textile Waste Water Through The Adsorption By Pumice Used In Stone Washing', 15(3), pp. 8–13. doi: 10.1515/aut-2015-0012.
- Zarei, M., Pezhhanfar, S. and Someh, A. A. (2017) 'Removal of acid red 88 from wastewater by adsorption on agro- based waste material . A case study of Iranian golden Sesamum indicum hull', *Kerman University of Medical Sciences*, 4(4), pp. 195–201. doi: 10.15171/EHEM.2017.27.
- Zarrabi, M. (2012a) 'Environmental Health Application of acidic treated pumice as an adsorbent for the removal of azo dye from aqueous solutions : kinetic , equilibrium and thermodynamic studies', pp. 1–10. doi: 10.1186/1735-2746-9-9.
- Zarrabi, M. (2012b) 'Environmental Health Application of acidic treated pumice as an adsorbent for the removal of azo dye from aqueous solutions : kinetic , equilibrium and thermodynamic studies', doi: 10.1186/1735-2746-9-9.

Appendix i

Table 8: Data of contact time

Using pumice		%	Using scoria	
Time(min)	Ct		Ct	%
5	30.1±32.2	37.5±37.8	34.1±34.3	31.4±31.7
15	16.5±16.8	64.2±64.4	20.2±20.5	59.2±59.5
30	7.01±7.3	85.6±85.8	8.1±8.4	83.2±83.4
60	4.2±4.8	91.6±91.9	6.4±6.7	86.2±82.5
90	1.4±1.9	96.4±96.8	4.4±4.6	90.4±90.6
120	1.3±1.8	96.5±96.9	2.1±2.6	95.6±95.7
150	1.6±1.9	96.1±96.4	1.5±1.7	96.1±96.3
180	1.7±1.9	96.2±96.5	1.6±1.8	96.3±96.2
210	1.6±2.0	96.1±96.6	1.4±1.6	96.3±96.4

Table 9: Data of effect of pH

pH	Using pumice		Using scoria	
	Ce	%	Ce	%
3	1.33±1.52	96.7±96.9	2.11±2.3	95.5±95.7
4	1.81±1.93	96.2±96.5	2.4±2.6	95.1±95.6
5	3.2±3.5	93.1±93.4	2.5±2.7	94.4±94.8
6	5.12±5.34	89.2±89.5	4.3±4.6	91.01±91.3
7	7.6±7.9	84.1±84.4	6.3±6.7	87.1±87.3
8	11.23±11.54	77.01±77.3	10.1±10.4	79.7±79.9
9	17.4±17.9	64.2±64.5	15.6±15.8	68.3±68.5
10	21.45	57.1±57.7	19.6±19.8	60.1±60.3

Table 10: Effect of initial concentration of direct black 22dye

Using pumice			Using scoria	
Co	Ce	%	Ce	%
5	0.15±1.18	96.4±96.6	0.21±0.24	95.3±95.8
10	0.36±0.38	96.1±96.3	0.46±0.49	95.1±95.5
20	0.86±0.89	95.4±95.6	1.02±1.3	94.4±94.8
50	2.43±2.46	95.1±95.5	3.1±3.5	93.5±93.7
100	10.7±10.9	89.1±89.5	10.4±10.8	89.2±89.6
150	43.03±43.06	71.3±71.6	36.3±36.9	75.4±75.9
200	80.6±80.09	59.4±59.9	64.4±64.8	67.6±67.9
250	132±134	46.5±46.8	155±159	53.8±54.1

Table 11: Data of effect dose of adsorbent

Doses	Using pumice		Using scoria	
	Ce	%	Ce	%
0.4	23.1±24.5	53.7±54.1	24.2±24.6	51.4±51.7
0.8	14.3±14.7	71.4±71.9	17.2±17.8	64.1±65.1
1.2	5.25±5.67	89.5±90.3	11.2±11.7	76.5±76.9
1.6	1.9±2.3	96.08±96.7	5.5±5.8	88.1±88.5
2.0	1.8±2.1	96.3±96.7	2.4±2.8	94.4±94.7
2.4	1.7±1.9	96.4±96.7	2.35±2.6	95.3±95.8
2.8	1.6±1.8	96.6±96.8	2.1±2.5	95.4±95.7

Table 12: Data of Effect of agitation time

Effects of agitation time at 200 rpm		
	Pumice	Scoria
Time	%	%
5	41.5±42.7	39.3±39.8
10	58.6±58.9	48.1±48.7
15	68.2±68.9	57.5±57.9
30	94.4±96.7	93.4±93.7
45	93.02±93.4	93.2±93.6
60	92.4±92.8	92.3±92.6
90	91.1±91.5	91.2±91.4

Table 13: Desorption data

Data of desorption test using pumice and scoria (1 st -3 rd) round							
		using pumice		using scoria			
1 st	2 nd	3 rd	Average	1 st	2 nd	3 rd	Average
59.4	47.3	42.6	49.7	68.9	57.6	49.4	58.6

Table 14: Data for Langmuir and Freundlich models (for both linear and non-linear)

Co	Using pumice			Using scoria		
	Ce	Qe	Ce/qe	Ce	qe	Ce/qe
5	0.175	0.3	0.58	0.23	0.24	0.95
10	0.38	0.6	0.63	0.49	0.47	1
20	0.88	1.2	0.73	1.02	1	1.02
50	2.45	2.3	1.1	3.1	2.4	1.3
100	10.9	5.6	1.9	15.8	4.2	3.8
150	43.05	6.7	6.4	29.4	6.1	4.8
200	80.8	7.5	10.7	52.8	7.3	7.2
250	133	7.3	18.2	73.6	8.8	8.4

Table 15 : Data of pseudo first order

Using pumice					Using scoria			
Time (min)	log(qe-qt)	log(qe-qt)	log(qe-qt)	Average	log(qe-qt)	log(qe-qt)	log(qe-qt)	Average
5	0.2	0.4	0.6	0.71	-0.49	-0.9	-0.6	0.67
15	0.24	0.36	0.8	0.64	-0.72	-0.69	-0.68	0.59
30	0.2	0.5	0.94	0.54	0.07	0.55	1	0.54
60	0.17	0.53	0.8	0.5	-0.22	0.37	0.85	0.33
90	0.12	0.58	0.77	0.49	-0.5	0.19	0.72	0.13
120	0.11	0.6	0.67	0.46	1	-0.18	0.38	0.4
150	0.11	0.6	0.8	0.5	-0.65	-0.22	0.32	-0.18
180	-0.4	0.62	0.2	0.14	-0.58	-0.46	0.28	-0.25
210	-0.6	0.6	0.3	0.1	-0.6	-0.55	0.23	-0.3

Ta

ble 16: Data of pseudo second order

	Using pumice			Average	Using scoria			Average
	10mg/L	20mg/L	40mg/L		10mg/L	20mg/L	40mg/L	
t/qtmgmin/g	t/qt	t/qt	t/qt	t/qt mgmin/g	t/qt	t/qt	t/qt	
17.2	9.6	8.11	11.6	13.1	4.45	2.9	6.8	
34	25	15.68	24.8	31.9	7.8	4.7	14.8	
56	60	49.4	55.1	60	62.5	42.5	55	
107	113	91.5	101.2	109	113	64.19	95.3	
150	157	121	142.6	157	163	98.87	139.6	
200	203	163	188.6	203	206	143.4	184.1	
290	250	178	239.3	250	254	164	222.6	
333	290	198	273.3	295	300	197	264	
338	350	208	298.6	344	350	231	308.3	

Table 17: Data of intra-particle diffusion

Data of intra-particle diffusion		
pumice		Scoria
$t^{1/2}$	qt	Qt
2.23	1.18	0.97
3.87	2.01	1.85
5.47	2.68	2.6
7.74	2.84	2.7
9.48	3.01	2.8
10.95	3.02	2.99
12.24	3.01	3
13.4	3.01	3.01
14.4	3	3.02

Table 18: Data of real sample (Co= 62.2 mg/L)

Doses	Using pumice		Using scoria	
	%	Ce	%	Ce
0.4	37.3	10.9	34.7	11.3
0.8	43.8	9.7	39.8	10.4
1.2	59.6	7.02	47.5	9.3
1.6	68.8	5.4	55.6	7.7
2.0	74.8	4.3	61.3	6.7
2.4	79.7	3.5	69.8	5.2
2.8	88.4	2.01	79.4	3.3

Table 19: Data of effect of interfering Anions

Anions	% removal of DB 22dye	% removal using scoria(direct black 22 dye)
Cl ⁻	55.6	49.7
SO ₄ ²⁻	64.1	64.2
NO ₃ ⁻	73.4	73.1
HCO ₃ ⁻	76.6	75.7
PO ₄ ³⁻	61.5	55.6
F ⁻	53.2	47.8
Mixture	33.2	29.6
Without	96.01	95.5

Appendix ii

Some procedures to characterize the waste water sample

Determination of phosphate

Stannous Chloride

The following volume of standard phosphate solution was separate into 100 mL volumetric flasks

Standard	Phosphate Solution(mL)	Phosphate (PO_4^{3-}) $\mu\text{g}/100 \text{ mL}$
	0	0
	1	5
	2	10
	3	15
	4	20
	5	25
	6	30

1. To the sample, add 0.05 ml 1 drop of phenolphthalein indicator solution and strong nitric acid to discharge to color
2. With a measuring pipette, add 4 mL acid- molybdate solution to each of the standards and sample
3. Mix thoroughly by inverting each flask four to six times.
4. With medicine dropper, add 0.5 mL (10 drops) of stannous chloride solution to each of the standards and sample.
5. Invert each flask four to six times

6. After 10 minutes, but before 12 minutes, measure the color photo metrically at 690 nm using distilled water as blank.

Determination of Chloride

Argentometric Method

1. Take sample (10 ml to 50 ml), add 2 ml of hydrogen peroxide (H₂O₂), add 2 ml K₂CrO₄ (potassium chromate indicator), titrate with silver nitrate (0.0141N).
2. To the color comparison, blank carefully add from a burette drop-by-drop silver nitrate titrant until the yellow color changes to a brownish tinge.
3. Record the mL silver nitrate titrant consumed.
4. If the sample turns yellow, gradually add silver nitrate titrate from a burette. Shake the Flask continuously and continue adding the titrant until the sample turns the same Orange- red color as in the color comparison blank.
5. Record mL silver nitrate titrant consumed.

Calculation

$$\text{Chloride (mg/l)} = \frac{(A-B) \times N. \text{ of silver nitrate} \times 35.45 \times 1000}{\text{volume of sample}}$$

A = ml titration for sample

B = ml titration for blank

N = normality of AgNO₃

Determination of biochemical oxygen demand (BOD)

Procedure

1. Take 5L of distilled water, aerated for 3.5 hours, added nutrients 1 ml nutrient for 1L aerated distilled water (FeCl, CaCl₂, MgSO₄, domestic water), aeration for 30 minutes.
2. BOD bottle (300 ml), add sample, fill the bottle with aerated water, put the lid (avoid air bubbles), keeping BOD incubator at 20°C for 5 days, after 5 days take the bottle and add 2 ml MnSO₄, 2ml alkalized iodide and 2 ml conc. H₂SO₄. Shake the bottle well (yellow colour) take 200 ml sample add starch solution as indicator (purple colour) titrated with 0.025 N sodium thiosulphate end point colour change from purple to colorless. In blank filled the bottle with aerated water without the sample and follow the procedure.

Calculation

$BOD_5 = (\text{blank value} - \text{titrated value}) \times 300 / \text{volume of sample}$

FLUORIDE

Alizarin Photometric Method

1. Prepare the following series of fluoride standards by measuring the indicated volumes of the standard fluoride solution into separate 100 mL graduated cylinders

Standard	Fluoride Solution. mL	Fluoride mg/100 mL
0		0
0.5		5
1.0		10
2.0		20
4.0		40
6.0		60
8.0		80
10.0		100

2. Add distilled water to the 100 mL mark, and mix by inverting each cylinder four to six times.

3. Measure the appropriate sample volume for the indicated fluoride range:

Standard	Volume mL	Fluoride Range mg/L
100		0.1-1.2
50		1.3-2.4
25		2.5-4.8

1. Place the clear and colorless sample in a 100-graduated cylinder. If necessary dilute to the 100 mL mark with distilled water and mix.
2. Remove any residual chlorine from the sample by adding 0.05 mL (1 drop) of sodium arsenate solution for each 0.1 mg of residual chlorine present in the sample and mix
6. Allow the standards and sample to come to the same temperature, because the color

Development depends critically on temperature. Adjust the temperature of samples and standards so that deviation among them is no more than 2^oc

7. With a volumetric pipette, add 5 mL Alizarin Red reagent & 5mL acid zinconyl Reagent to each of the standards and the sample. Complete the addition of reagent to the entire series of cylinders within 5 minutes.
8. Mix the contents by inverting four to six times
9. Allow to stand for at least 1 hour \pm 5 minutes
10. Measure the standard and sample absorbance at 550 nm using distilled water to zero the spectrophotometer.
11. Construct a calibration curve using the standard series
12. From the calibration curve determine the microgram fluoride in the sample making the necessary blank correction

$$\text{mg/L F} = \frac{\text{mg F}}{\text{ml of sample}}$$

SULFATE

Gravimetric Method with Ignition of Residual

- 1) Adjust the volume of clarified sample to contain approximately 50 mg of sulfate in a 250 ml volume. Lower concentrations of sulphates may be tolerated if it is impractical to concentrated the sample to the optimum level, but in such cases limit the total volume to 150 ml
- 2) Adjust the pH with concentrated HCl to pH 4.5-5.0 using a pH meter or the orange color of methyl red indicator. Then, add an additional 1 to 2 ml HCl.
- 3) Heat the solution to boiling and while stirring gently, add warm barium chlorides solution slowly until precipitation appears to be complete. Then add about 2 ml in excess
- 4) Digest the precipitate at 80-90 ^oC for not less than 2 hours.
- 5) Filter and wash the precipitate with small portion of warm distilled water until the washings are free of chloride as indicated by testing with AgNO₃-HNO₃ reagent. Be sure that all of the precipitate is transferred to the paper.
- 6) Place the filter paper and precipitate in ignited and weighed crucible and dry in the oven
- 7) Ignite at 800^oC for 1 hour, cool in a desiccators and weigh.

8) Calculation: $\text{mg/L SO}_4^{2-} = \text{mg BaSO}_4 \times 411.6 \text{ Ml sample}$

CHEMICAL OXYGEN DEMAND

Open Reflux Method, Titrimetric Method

1. place 5 ml of sample in a 250 or 500 ml refluxing flask
2. Add about 3 glass beads to the reflux flask.
3. Add approximately 1 g mercuric sulfate
4. Very slowly add 5.0 ml sulphuric acid reagent with mixing to dissolve the mercuric sulfate.
5. Cool under the tap while mixing to avoid possible loss of volatile materials.
6. Add 25.0 ml of 0.0417M (0.25 N) potassium dichromate solution
7. Mix until the solution is completely homogeneous.
8. Attach the reflux flask to the condenser and turn on the cooling water
9. Add 75 ml of sulphuric acid reagent through the open end of the condenser Continue swirling and mixing while adding the sulphuric acid reagent
10. Cover the open end of the condenser with a small beaker and reflux for exactly 2 hours.
11. Cool, and wash down the condenser with about 50 ml of distilled water
12. Cool to room temperature under a tap and mix well.
13. Titrate the excess $\text{K}_2\text{Cr}_2\text{O}_7$ with ferrous ammonium sulfate(FAS) titrant using 2 to 3 drops of Ferroin indicator taking the end point of the titration the first sharp color change from blue-green to reddish brown
14. In the same manner, reflux and titrate a blank containing the reagents and 50 ml of distilled water.
15. Calculation:

$$\text{COD as mg O}_2/\text{L} = \frac{(\text{A}-\text{B}) \times \text{M} \times 8,000}{\text{ML of sample}}$$

Where A= ml FAS used for the blank

B= ml FAS used for sample

M= Molarity of FAS